WADC TECHNICAL REPORT 54-17
PART 2

JOINING OF MOLYBDENUM

W. N. PLATTE

WESTINGHOUSE RESEARCH LABORATORIES

NOVEMBER 1955

WRIGHT AIR DEVELOPMENT CENTER

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NOVEMBER 1955

MATERIALS LABORATORY
CONTRACT No. AF 18(600)-114
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WRIGHT AIR DEVELOPMENT CENTER
AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

Carpenter Litho & Prtg. Co., Springfield, O.
400 - April 1956

FOREWORD

This report was prepared by the Westinghouse Research Laboratories under USAF Contract No. AF 18(600)-114. This contract was initiated under Project No. 1252, Task No. 73012, "Joining of Molybdenum," formerly RDO No. 446-48, and was administered under the direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center, with Lt T. Hikido acting as project engineer.

This report covers work conducted from September 1953 to September 1954.

ABSTRACT

A study of the factors which influence the physical properties, especially the ductility, of molybdenum welds is discussed in this report. Welds in both arc-cast and vacuum sintered molybdenum made in commercially pure inert atmospheres and in contaminated inert atmospheres are examined.

The effects of several deoxidizers on the welding properties of vacuum sintered molybdenum are examined. The specific requirements of deoxidizing agents are established and it is shown that titanium between 0.2 and 0.5% meets these requirements.

The effects of interstitial elements, oxygen, nitrogen and carbon, on the weld properties of arc-cast molybdenum have been examined. It is shown that the limits for oxygen in the inert gas welding atmosphere can be predicted. The deleterious effects of nitrogen and oxygen are shown quantitatively by means of bend test data. Both oxygen and nitrogen reduce the ductility of molybdenum weld metal. Carbon is also believed to have a similar effect.

Oxygen and nitrogen are shown to have an interaction effect when used in combination in the inert welding atmosphere. Nitrogen reduces the deleterious effects of oxygen and vice versa, but the combination is not as effective as high purity inert gas as a welding atmosphere.

Exploratory studies are described for slightly improved inert gas atmospheres and post-weld heat treatment. Butt welds were made to establish the validity of using "bead on plate welds" as a test criterion.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

M. R. WHITMORE
Technical Director
Materials Laboratory
Directorate of Research

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I INTRODUCTION

Welded molybdenum joints have been formed using a number of the existing processes. However, operating limitations and joint quality restrictions occur in welds made by the known welding methods. Molybdenum's ability to form oxides eliminates all of the fusion welding processes with the exception of the inert gas arc. Unfortunately, porosity, hot cracking and low ambient temperature ductility have been characteristic of fusion welds made by this process in the past. Flash-butt welds have been made in molybdenum, but this application is limited to butt joints in plates or bars, and the quality and ductility depend upon the material to be welded. The percussive welding process has been used with success on a type of molybdenum not weldable by the other processes. This process is limited to butt joints and the nature of the process limits it to small sections. Furthermore, commercial equipment is not readily available. The spot welding process has been used but the short life of the electrodes is prohibitive and only lap joints can be formed.

The inert gas shielded arc process was selected for study in these investigations because of its flexibility. At the beginning of the investigations it was believed that suitable selection and improvement of material would overcome the hot cracking and porosity found in welds made by this process. Experimental work has confirmed this prediction.

Molybdenum and most other body centered cubic materials are subject to a rise in the yield strength when the temperature is decreased. Brittle fracture occurs when the yield strength reaches the fracture strength of the material. Bechtold[1] has shown that the fracture strength is dependent upon the grain size. This work explains in part the difficulties encountered in fusion welding molybdenum. Perry, Spacil and Wulff[2] suggest that the grain boundaries of molybdenum are wet by a eutectic of MoO_3 and Mo at temperatures in the welding range. They also show that MoO_3 is sufficiently volatile above 3800°F to cause porosity. The combination of large grain size and grain boundary precipitates may explain the low ductility found in molybdenum fusion welds. Porosity and hot cracking can also be explained by oxides in the weld metal. The work of Battelle investigators[3,4] showed that the impurity content of cast molybdenum must be held at a minimum if a ductile material is to be obtained. It is apparent that if sound ductile weld metal is to be obtained the material must have a low initial impurity content and

the acquisition of impurities during welding must be minimized. Previous work[5] has emphasized the importance of pure material. Welds made in commercial sintered molybdenum cracked and developed porosity during welding under high purity atmospheres while carbon deoxidized molybdenum was free of both these defects.

A multiple approach was used toward the solution of the problem of obtaining sound welds with a degree of engineering ductility. Improved sintered molybdenum was examined to determine its requirements for welding. Carbon deoxidized arc-cast molybdenum was used to determine the effects of the welding atmosphere purity upon the weld quality and ductility. Oxygen and nitrogen additions were made separately and in combination to the argon welding atmosphere in controlled amounts, and the welds were examined to determine the effects of these impurities upon the properties of the welds. Interaction relationships were studied between these two gases when they were added in combination.

II MATERIAL

The major portion of the work on welding atmospheres was done on carbon deoxidized arc-cast molybdenum. This material was obtained from the Climax Molybdenum Company and came from a single ingot. The material was reduced to 0.060 inch sheet according to the grain size control program developed by Bechtold.[1] The sheet had a uniform fine fibered structure in the "as worked" condition.[5] This material recrystallized at 1300°C in one hour. By check analysis the material contained 0.0018% oxygen, 0.003% nitrogen and 0.06% carbon. The final rolled cross-section dimensions of the sheet were 0.060 in. x 7 in. Weld test plates were cut from the strip in pieces 2 in. x 7 in. perpendicular to the length of the sheet so that the weld test beads could be made perpendicular to the final direction of rolling.

A second lot of arc-cast molybdenum was used for weld tests. This material had been deoxidized with aluminum, Table I. The rolling procedure was the same as for the carbon deoxidized material. Metallographic examinations have not been completed.

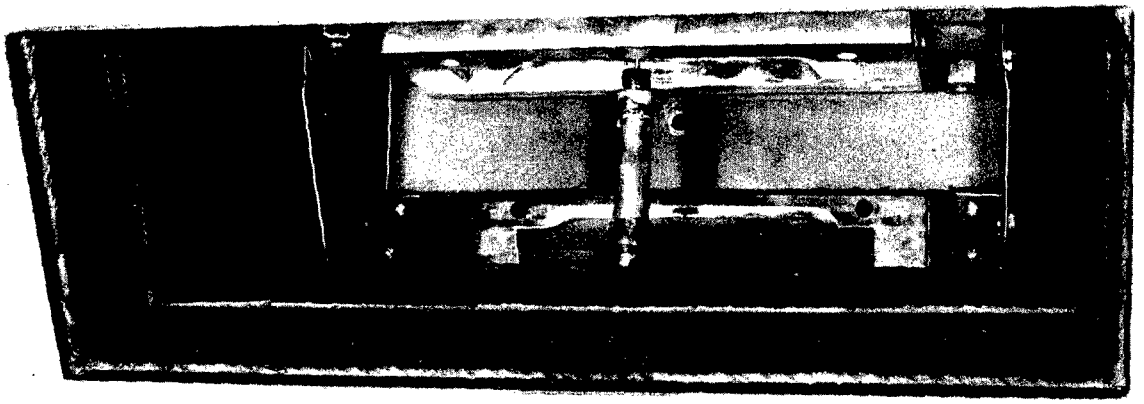

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Fig. 1 - Interior-Arc Chamber

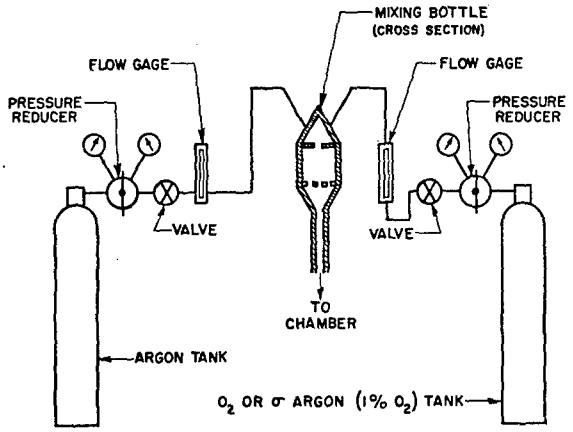

Fig. 2

Schematic-Gas Mixing System

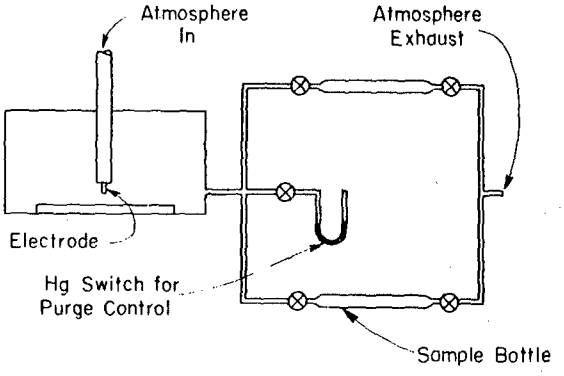

Fig. 3

Schematic of Gas Sampling System for Welding Chamber

A third lot of molybdenum was received which had been deoxidized with carbon, Table I. As yet welds have not been made in this material.

TABLE I

ANALYSES OF ARC-CAST MOLYBDENUM

Lot No.	Deoxidizer	Al	Fe	Ni	W	As	Mn	Mg	Pb	Sn	Si	C
2	Al	0.16	0.011	0.011	0.04	0.0002	0.002	0.002	0.005	0.005	0.005	0.01
3	C	0.04	0.010	0.009	0.02	0.0002	0.002	0.002	0.005	0.005	0.005	0.04

Vacuum sintered molybdenum samples deoxidized with several different agents were examined for their welding properties. The deoxidizing agents used were Ti, Ta, Nb, Al, C, and Zr. The detailed analysis of these materials will be discussed later together with their welding characteristics.

III EQUIPMENT

A number of modifications and additions were made to the equipment described in the first annual report.[5] The welding chamber and auxiliary equipment are shown in Figs. 1-3. The welding chamber operates at a positive pressure of approximately 30 mm of Hg. The system consists of gas shielded arc operating in an atmosphere of the same gas. This is accomplished by causing the welding atmosphere to enter around the tungsten electrode during welding, and after the chamber has been purged of its original atmosphere. The atmosphere around the welding arc can be controlled at all times. Any gases liberated during welding are removed by the incoming atmosphere. This system also has an advantage in welding materials such as molybdenum which have volatile oxides. Any oxide formed or liberated is swept away by the welding atmosphere entering around the electrode.

The composition of the atmosphere supplied to the chamber may be

varied as desired. A gas-mixing system is used to pre-mix the gases before they enter the chamber. A schematic drawing of the mixing system as used for two gases is shown in Fig. 2.

The chamber is purged by passing gas of the desired composition from the mixing system into the chamber. When the pressure in the chamber reaches 30 mm of Hg, the gas supply is automatically stopped and the chamber is evacuated to a pressure slightly below atmospheric. The pumping time is 1/2 minute. At the end of the pumping period the gas flow is resumed. This process is repeated 30 times. During the purge period a rubber bellows provides a breathing action such that the 30-cycle purge leaves the chamber free of all gases except those supplied to it. After the purge period the pump is shut off and an exhaust is opened. The welding atmosphere gases are supplied at a rate equivalent to the exhaust so that a positive pressure is maintained. The gas flow used was 27.5 cu ft/hr. It was found that the atmosphere in the chamber was equivalent to the purity of the gas supplied through the mixing unit.

The atmosphere in the chamber was sampled using the system shown in Fig. 3. Gas sampling bottles were placed directly in the exhaust line of the chamber. Two sample bottles provided samples before and after welding. Other exhaust lines are parallel to those shown so that the gas flow is not interrupted by sampling. Gas samples were analyzed by means of a mass spectrometer.

Welding was accomplished by use of a direct current tungsten arc. The welding current was supplied by a Westinghouse RA rectifier welder, Style 1458540. The molybdenum plate was used as the anode. This arrangement places the major portion of the heat at the plate. Welding current was maintained at 180 amps for the 0.060 molybdenum sheet. A spark gap oscillator, Westinghouse Style 1547011, was used to provide a high frequency spark for arc initiation. The welding current and voltage were recorded on an Esterline Angus recorder.

The tungsten electrode used was 3/32 inch in diameter and the distance between the electrode and the plates was maintained at 3/32 inch. The plate was moved relative to the electrode by means of a screw drive unit so that a constant travel speed was maintained without manual manipulation of the electrode during welding. The drive screw was

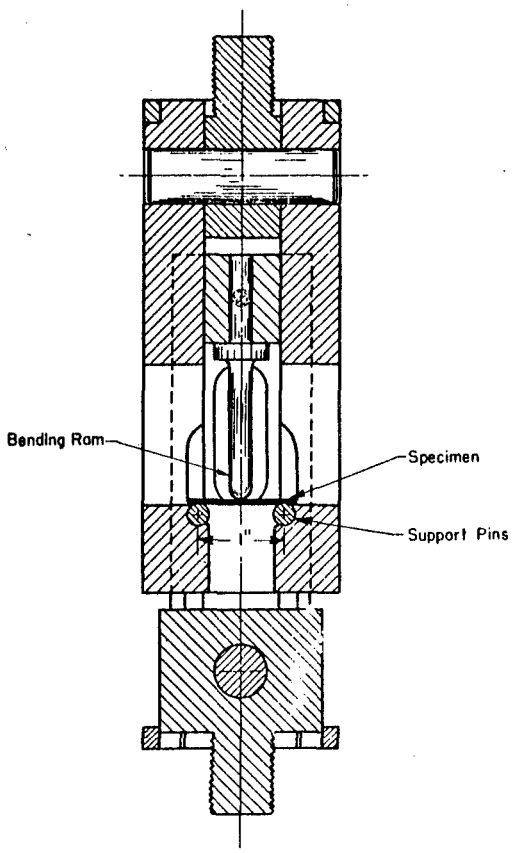

Fig. 4 Bend Test Fixture

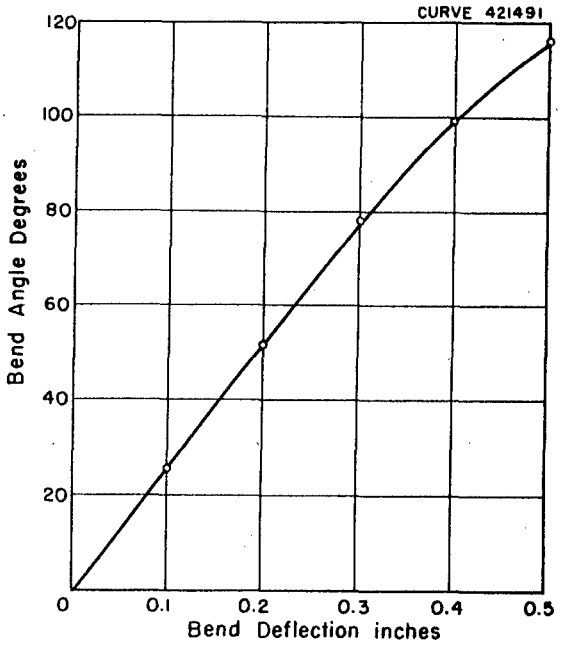

Fig. 5 Relationship Between Bend Deflection and Angle of Bend

operated by means of a Graham variable speed drive unit. The arc travel speed was held at 5.9 to 6.2 inches per minute and was constant for any given weld.

Guided bend tests were used to determine the ductility of the weld metal. A constant strain rate machine with a special bend test fixture was used for all testing in these investigations, Fig. 4. This test device required a sample 0.060 x 0.250 x 1.125 inches. The samples were ground to zero taper tolerances. The specimen is placed in the test fixture with the weld bead in the position of maximum fiber stress. The rate of advance of the bending ram in this fixture was six inches per hour, which gives a strain rate on the outer fiber of the specimen of 0.0183 inch per minute. This strain rate was computed for elastic strain and the true strain rate will change beyond the elastic limit. The data from bend tests are given in inches of deflection. The deflection of the sample

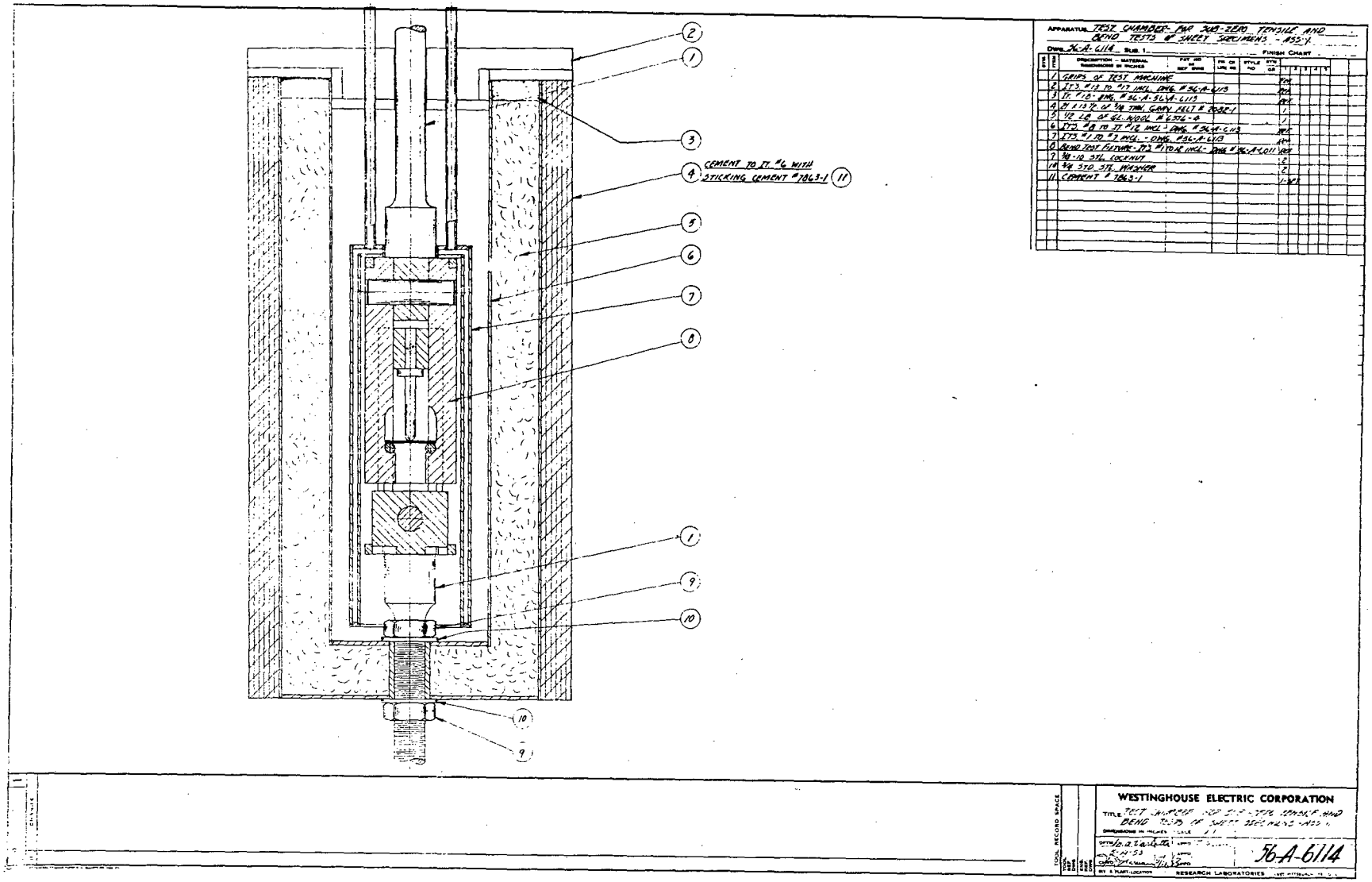

Fig. 6 - Test Chamber for Sub-zero Tensile and Bend Tests on Sheet Specimens.

has been correlated with the angle of bending so that these data can be compared with the work of other investigators, Fig. 5.

Testing at temperatures above ambient was accomplished by means of a conventional type tube furnace controlled to ±5°F and having a maximum temperature gradient of ±5°F over the test zone. Testing below ambient temperatures was accomplished with the special low temperature chamber, Fig. 6. The chamber is shown with the bend test fixture in position. The temperature of the specimen is controlled in both cases by means of a thermocouple placed in the center of the bending ram at its point of contact. In the low temperature chamber the thermocouple controls a solenoid valve which allows liquid nitrogen to pass into the double-walled inner cylinder. The nitrogen may be liquid or gaseous depending upon the flow rate required to maintain the desired temperature. The nitrogen passes through the perforations in the inner wall of the double-walled chamber, and the cold gas flows downward past the sample and bend test fixture and works its way out the bottom of the double-walled can and ultimately out of the chamber. This device is a modification of a similar unit described by Wessel and Olleman.[6]

In the low temperature chamber and in the tube furnace the sample is always surrounded with a gaseous medium. This eliminates the possible errors which may result when tests are made in a medium which wets the sample as shown by Benedicks.[7]

In conjunction with the sintered molybdenum portion of the welding program a molybdenum furnace muffle was fabricated. A drawing of the furnace muffle is shown in Fig. 7. The muffle is 56 inches long and 4-1/4 inches square with one end sealed. The molybdenum sheet for the muffle was cut with a metal shaper and the flanged members were bent at 750°C (1382°F). One of the flanged members was curved after bending. An attempt to cold straighten the part caused it to crack. A duplicate member was made and it also curved. Since there was no additional material available, and this part had sufficient ductility to be forced to fit the other parts, it was welded into the muffle.

The side sections were clamped together and tack welded at 3-inch intervals. The tack welding was done in a chamber previously pumped down to 10^{-5} mm of Hg and then filled with high purity helium. The weld tacks

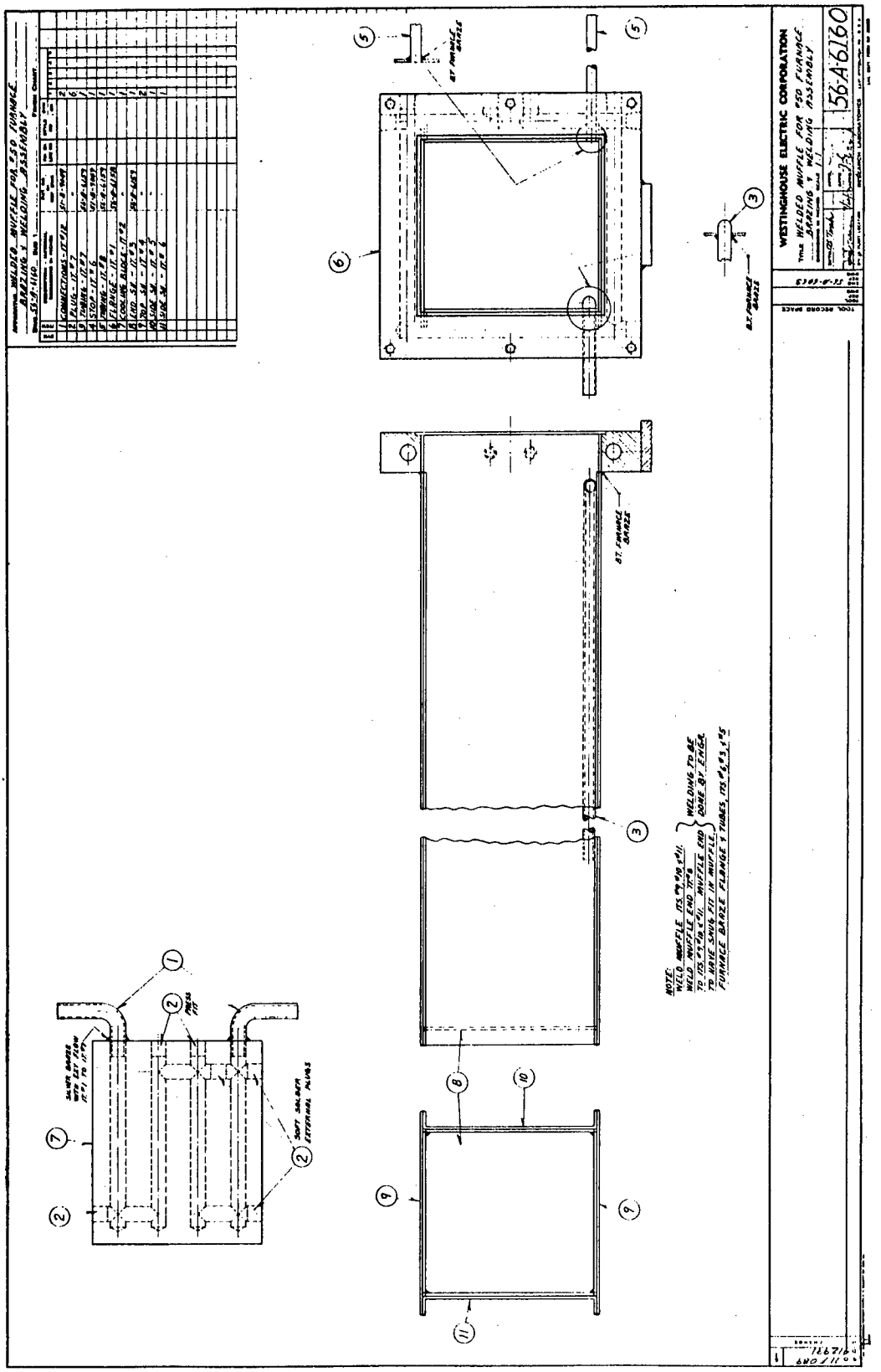

Fig. 7 - Welded Furnace Muffle

were 1/4 to 1/2 inch long. A crack developed in the flanged member which had been distorted in bending the flanges. The nature of the crack indicated the presence of oxides in a lamination in the flange. Residual distortion stresses may also have contributed to the cracking but the principal cause was the oxide. Tacking was done from one end of the muffle to the other along alternate corners.

The muffle was removed from the chamber after tacking. The clamps were removed and the weld areas were cleaned with a wire brush and acetone. The muffle was then replaced in the chamber for welding.

The welding sequence used is shown in Fig. 8. Welding was done in the order: 1A, B, C, D; 2A, B, C, D; 3A, B, C, D. The object of this sequence was to leave a minimum of residual stresses in the center of the muffle. Welding was done in the same type helium atmosphere used in the tacking operation. During welding a number of cracks developed in the flanges of the member which had been distorted to obtain a satisfactory fit up. No cracking occurred in the undistorted piece.

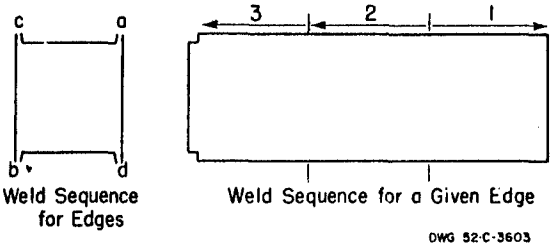

Fig. 8 - Welding Sequence for Molybdenum Furnace Muffle.

After the edges had been welded the muffle was placed in a second chamber and the end plate was welded manually. The same type of high purity helium atmosphere was used, but, due to welding distortion, filler metal was required in the end plate joints. Cracking did not occur in these joints.

Cracks in the flanged member were repaired by a re-melting process where possible. However, several cracks required filler metal additions. The end plate welds and a portion of the edge welds are shown in Fig. 9. A repaired crack is shown in Fig. 10.

The difficulties encountered while welding the furnace muffle emphasize two important welding factors. First, in molybdenum fabrication the surfaces to be welded must be free of oxides and oxide-containing laminations; second, residual stresses in the material prior to welding must be low. The furnace muffle cracks can be traced directly to these two factors.

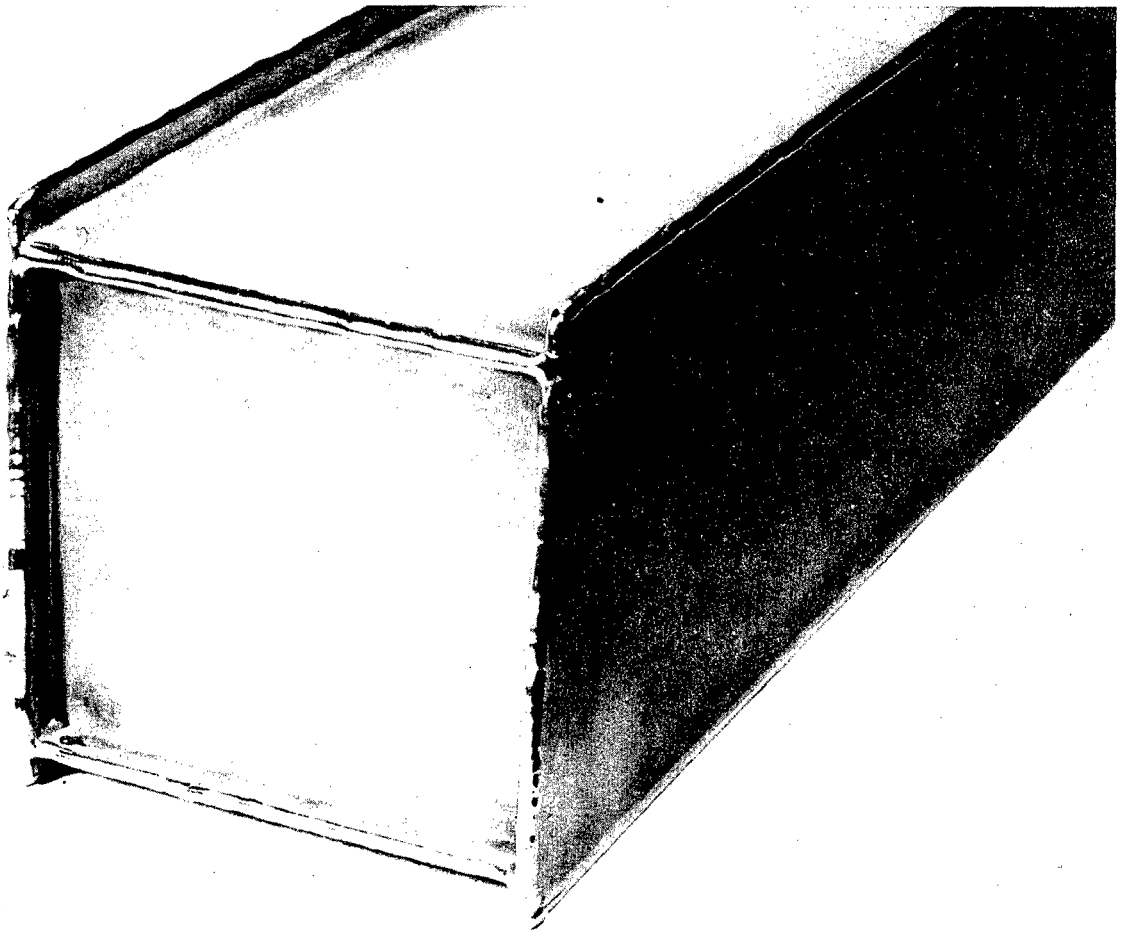

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Fig. 9 - End Plate in Furnace Muffle

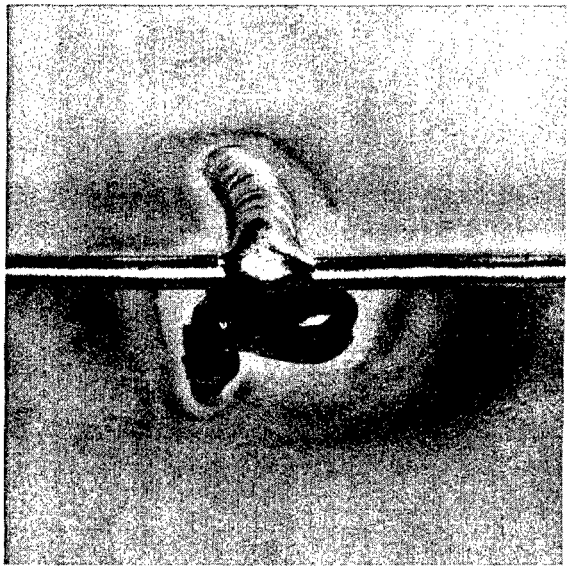

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Fig. 10 - Repaired Crack in Furnace Muffle

After welding, the muffle was given a stress relief heat treatment at 900°C for four hours in a vacuum. The muffle was cooled from 900°C to approximately 250°C in 15 hours. A higher stress relief temperature would have been preferred but the furnace available was incapable of reaching temperatures above 900°C.

IV SINTERED MOLYBDENUM

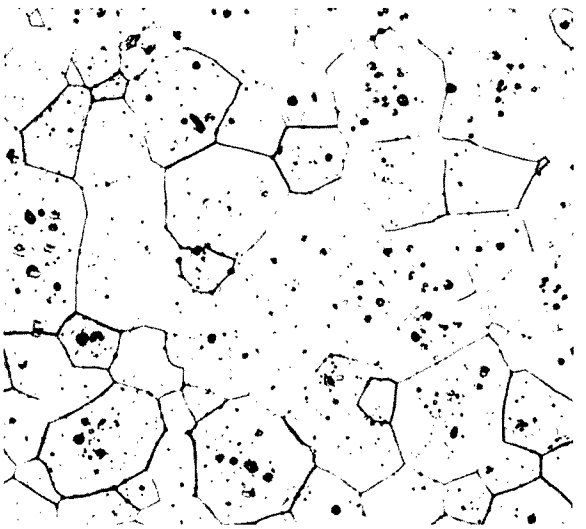
Commercial sintered sheet was used by many of the early investigators in studying the welding properties of molybdenum.[5,8,9] The high oxygen content of this material made its welding properties unsatisfactory as shown in the first annual report on Joining Molybdenum.[5] Welds in commercial sintered molybdenum show gross hot cracking and porosity. One objective of the present investigation was to procure and evaluate improved sintered molybdenum as it became available. In the course of the past year a number of vacuum sintered deoxidized heats of molybdenum were welded and the welding characteristics and mechanical properties of the welds were studied. The effectiveness of Ti, C, Al, Ta, and Nb as deoxidizers was examined with respect to the welding characteristics. Previous work showed that these deoxidizers might improve weld quality in sintered molybdenum.

Titanium Deoxidized Molybdenum

The first lot of titanium deoxidized molybdenum was obtained to determine the range of titanium additions which gave a material with the best welding properties. The vacuum sintered material used for these welding studies was prepared in laboratory lots. Earlier work at the Westinghouse Research Laboratories has shown that molybdenum powder freshly reduced will acquire up to 10% of its total oxygen pick-up when exposed to air for a few minutes. With this knowledge as a background the powder used for vacuum sintered samples was first reduced in dry hydrogen. The powder was removed from the furnace and placed in sealed

containers with the deoxidizer. The containers had previously been flushed with argon. The deoxidizer and freshly reduced molybdenum powder was mixed in the argon-filled container for 16 hours by rotating the container in a horizontal position. The powder was then removed and pressed into compacts and placed in the vacuum sintering furnace. The total exposure to air was five minutes or less.

Difficulty was experienced in mixing the titanium powder. For safety reasons the powder is supplied with a 20% water content. The early heats of titanium deoxidized molybdenum were made with wet titanium powder. These samples showed a tendency for the titanium to agglomerate and form inclusion streamers in the material.



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200X

Fig. 11 - Typical Sintered Molybdenum With 0.5% Ti Addition. Sintered 4 Hrs. at 3812°F (2100°C)

The compressed compacts were approximately 3-1/2 in. x 1-1/2 in. x 3/4 in. After sintering at 1950° to 2100°C for four hours the compacts were 3 in. x 1-1/8 in. x 0.6 in. The compacts were cross rolled to a transverse section of 2 in. x 0.060 in. The rolling and sintering data are given in Table II. Rolling was done in eight passes with intermediate reheats to 1100°C. The initial reduction was 10% and the total reduction was 85%. A typical photomicrograph of an as-sintered compact is shown in Fig. 11.

The sintered molybdenum heats shown in Table II were welded in the chamber, Fig. 1, using welding grade argon as an atmosphere. The welding data and atmosphere analyses are given in Table III. Photographs and X-ray pictures of two typical welds appear in Figs. 12-13. These pictures give visual evidence of the beneficial effect of titanium as a deoxidizer for vacuum sintered molybdenum. Gross cracking occurred in the control sample vacuum sintered without a deoxidizer addition, Fig. 12. This sample also showed evidence of porosity. The welds in material

TABLE II

VACUUM SINTERED TITANIUM DEOXIDIZED MOLYBDENUM

(LOT NUMBER 1)

Sample No.	Plate Analysis	Sintering Time	Sintering Temp.	Final Thickness In.
WS162	Ti 0.20 N 0.004 C 0.05	Vacuum 4 Hr	3812°F	0.058-0.059
WS163	Ti 0.46 N 0.004 C 0.01	Vacuum 4 Hr	3812°F	0.059
WS159	Ti 1.87 N 0.014 C 0.04	Vacuum 4 Hr	3812°F	0.059
WS165	Ti 1.88 N 0.010 C 0.04	Vacuum 4 Hr	3812°F	-

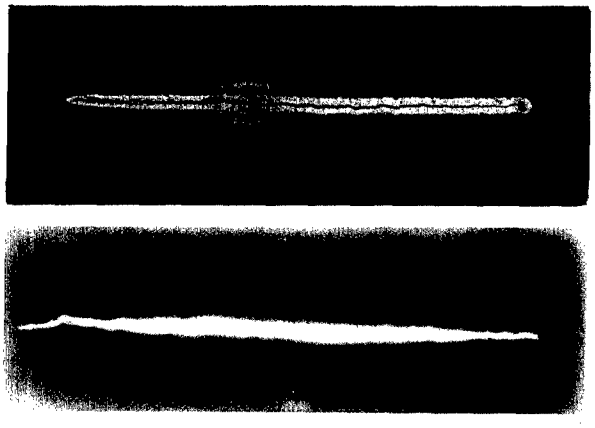

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Fig. 12 - Weld in Vacuum Sintered Pure Mo Welded in Argon. WS158

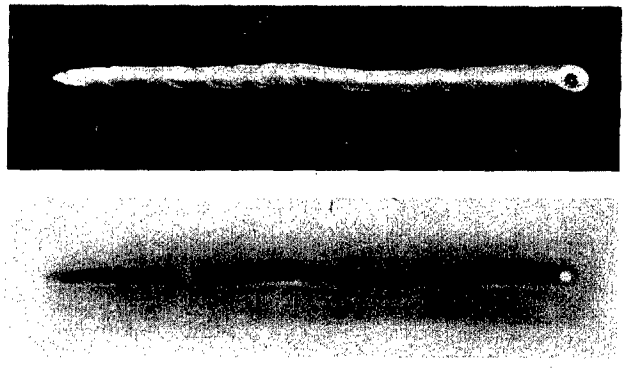

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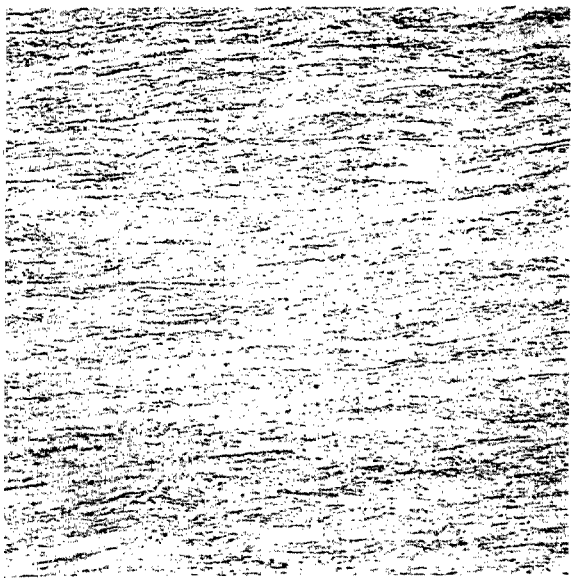
Fig. 13 - Weld in Vacuum Sintered Mo, 0.2% Ti. Welding Atmosphere Argon. WS162

TABLE III

WELDING DATA FOR VACUUM SINTERED Ti DEOXIDIZED MOLYBDENUM

Sample No.	Material Analysis	Atmosphere Analysis	Current Amp	Voltage	Arc Travel Speed In./Min	Remarks
WS158	100% Mo	99.9% A 0.1% N_2	175	11.5	6	Clean, bright bead; crack full length.
WS159	1.87 Ti, Bal. Mo 0.014 N 0.04 C	99.9% A 0.1% N_2	175-180	13	6	Clean, bright, rough, with weld depression at side of bead near middle.
WS162	0.2% Ti, Bal. Mo 0.004 N 0.05 C	99.9% A 0.1% N_2	180	12.5	6	No cracks, clean, bright, black specks along edge of bead.
WS163	0.46 Ti, Bal. Mo 0.004 N 0.04 C	99.9% A 0.1% N_2	175	13.5-14	6	Clean, gray-silver, narrow bead.
WS165	1.88 Ti, Bal. Mo 0.01 N 0.04 C	99.9% A 0.1% N_2	185	12.5-13	6	No cracks, slag on bead, 100% penetration.
WS158A	100% Mo Annealed 1 hr 1200°C	99.9% A 0.1% N_2	178	12.5-13	6	Narrow, bright bead, crack full length.
WS162A	.2 Ti, Bal. Mo .004 N .05 C Annealed 1 hr 1200°C	99.9% A 0.1% N_2	178	13	6	Clean bead except for slag spots. No cracks.

deoxidized with titanium were sound and free of gross porosity. Samples containing 1.87% and 1.88% Ti showed material imperfections which are the result of titanium segregation in the sintered compact. The control sample, made without deoxidizer additions, shows grain boundary cracking and porosity, Fig. 14. A typical sample deoxidized with 0.2% Ti is shown in Fig. 15. The as-rolled material shows slight evidence of segregation of the titanium. There is no evidence of



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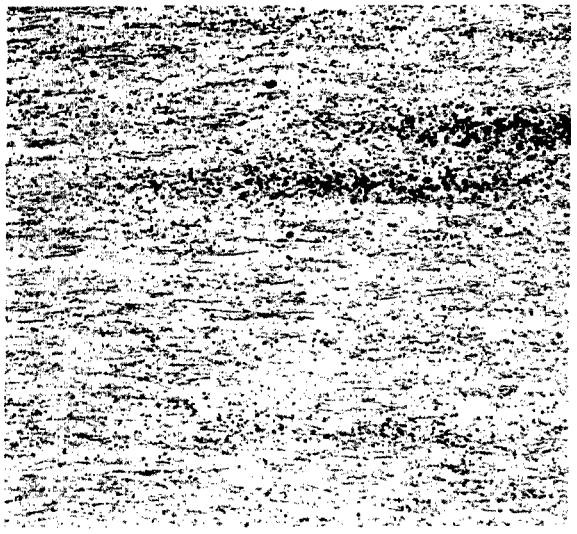
(a) As Rolled 100X

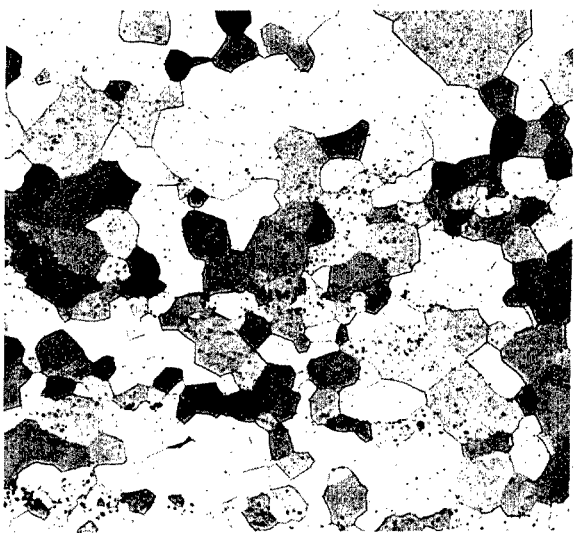
P-53-215-13

(b) Weld Zone 100X

Fig. 14 - Weld in Vacuum Sintered Molybdenum. No Deoxidizer Addition. WS158.

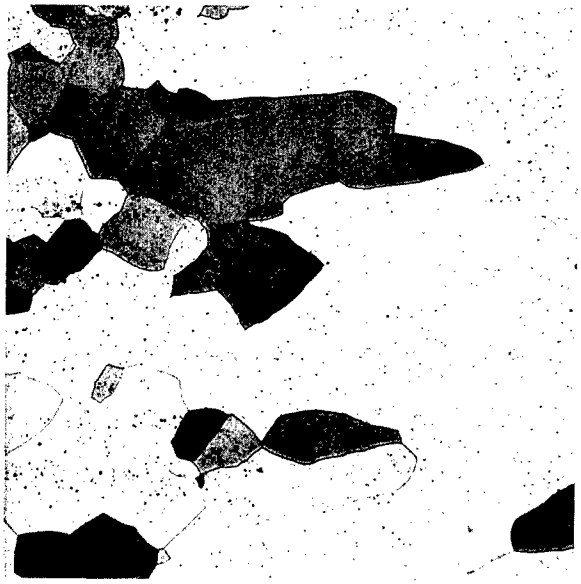


(a) As Rolled 100X

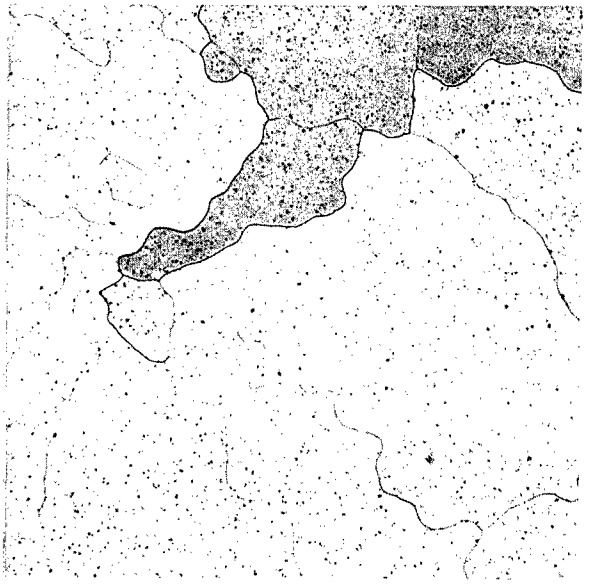


(b) Recrystallized 100X

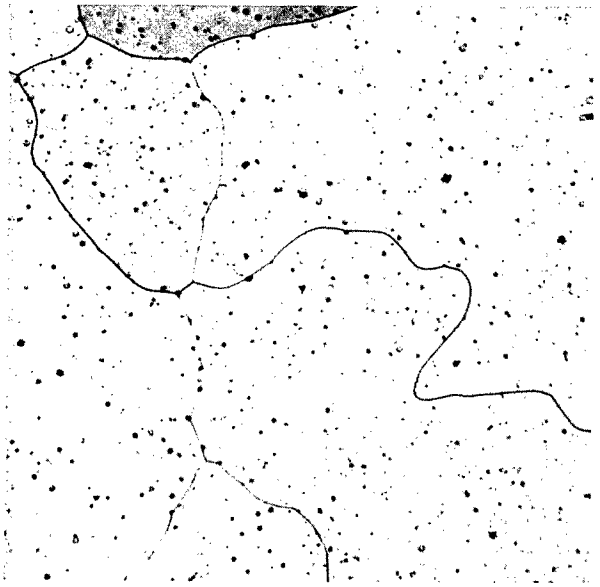
Fig. 15 - Weld in Vacuum Sintered Molybdenum. Deoxidized with 0.2% Ti. WS162. P53-214-1,3,4,5,6. (Continued)



(c) Edge of Weld 100X



(d) Center of Weld 100X



(e) Center of Weld 300X

Fig. 15 - Weld in Vacuum Sintered Molybdenum. Deoxidized with 0.2% Ti. WS162. P53-214-1,3,4,5,6. (Continued)

porosity at the edge of the weld zone. The center of the weld was free of cracks and porosity. The irregularity in the grain boundaries is most probably due to the existence of very fine precipitates which impede the local movement of the grain boundaries. The grain size in the welded area is relatively fine compared to arc-cast material discussed later. Similar results were found in a weld in 0.5% titanium deoxidized vacuum sintered molybdenum. Segregation of titanium appeared in the recrystallized material and the weld metal was finer grained. Welds made in sintered molybdenum deoxidized with 1.88% titanium show a tendency toward fine porosity. Marked segregation of titanium in the base metal sheet occurs in these materials. However, the grain size in the welded area was restricted by the addition of titanium.

The welds made in titanium deoxidized sintered molybdenum were cut into bend test specimens and tested over a range of temperatures in the test fixtures discussed earlier. The results of these tests are given in Table IV and Figs. 16 and 17. These data show that titanium as a deoxidizer for sintered molybdenum is best in the range 0.2% to 0.5%. Welds in this material did not become completely brittle until tested at -130 to -160°F and were ductile, that is, resulted in a 100° bend or 0.4 in. deflection, at 320°F. These results are comparable to some of the welds in arc-cast carbon deoxidized molybdenum discussed later. The welds in molybdenum sintered in vacuum and deoxidized with 1.88% Ti showed completely brittle behavior at 0°F and did not become fully ductile at temperatures below 400°F.

The relationship which exists between the stress in the outer fiber at the proportional limit and the test temperature is shown in Fig. 17. If the curves in Figs. 16 and 17 are compared with curves for the best welds obtained from arc-cast carbon deoxidized molybdenum, Fig. 18, it will be seen that the rise in the proportional limit occurs at a lower temperature in the sintered molybdenum than in the arc-cast material. There is an exception to this in the case of the sintered molybdenum deoxidized with carbon only. The stress at the proportional limit in this case is almost identical over the range of test temperatures used as was found for the arc-cast carbon deoxidized material. This condition suggests an effect due to the type of deoxidizer used rather than the degree of deoxidization. The welds in the titanium deoxidized material

TABLE IV

BEND TEST DATA FOR VACUUM SINTERED MOLYBDENUM WELDS DEOXIDIZED WITH CARBON AND TITANIUM

Sample No.	Chemical Composition %	Test Temp. °F	Thickness Inches	Width Inches	Load at Prop. Limit Lbs.	Max. Load Lbs.	Load at Fracture Lbs.	Stress at Prop. Limit PSI	Deflection Inches
WS160	C 0.10	400	0.046	0.249	9.5	31.4	-	27000	0.5*
	N 0.004	360	0.046	0.249	10.6	32.2	24.4	30000	0.375
		320	0.047	0.249	10.6	35.5	35	28700	0.257
		240	0.047	0.249	15.6	-	36.8	42400	0.160
		80	0.047	0.249	25.5	-	42.8	69200	0.107
		-80	0.047	0.249	50.3	-	57	137000	0.006
		-120	0.0465	0.249	-	-	58.5	162000	-
WS162	Ti 0.20	400	0.040	0.251	5	20	-	18700	0.5*
	N 0.004	360	0.045	0.251	8	24.5	-	23700	0.5*
	C 0.05	340	0.045	0.251	8	26.5	-	23700	0.5*
		320	0.039	0.251	7	18	15	27600	0.399
		240	0.041	0.250	7	22	20.5	26200	0.338
		160	0.045	0.250	17	-	19	50200	0.010
		79	0.043	0.251	13	-	27	42000	0.101
		0	0.043	0.250	24	-	37.5	78000	0.094
		-160	0.043	0.250	40	-	49	130000	0.002
		-200	0.043	0.2505	-	-	41	133000	0.000
WS163	Ti 0.46	320	0.054	0.248	13	43	-	27700	0.500*
	N 0.004	280	0.053	0.248	16	45	44	34200	0.314
	C 0.04	240	0.053	0.248	16	-	40.5	34200	0.122
		240	0.053	0.248	17.5	-	36	37300	0.069
		160	0.053	0.248	19	-	47	40500	0.131
		80	0.053	0.248	27	-	47	57600	0.068
		0	0.054	0.248	37	-	54.5	79000	0.028
		-80	0.054	0.248	54	-	70	98200	0.021
WS159	Ti 1.87	400	0.044	0.251	8.5	-	20.9	26300	0.097
	N 0.014	240	0.044	0.250	10.7	-	21.5	33200	0.061
	C 0.04	80	0.044	0.251	19.5	-	25	60500	0.014
		0	0.044	0.250	-	-	27.8	85500	0.000
WS165	Ti 1.88	480	0.0445	0.251	11.5	30.6	29	34000	0.292
	N 0.010	400	0.044	0.250	11	32	31.2	32500	0.259
	C 0.04	320	0.045	0.251	12.5	-	26.3	37000	0.054
		240	0.045	0.250	14	-	33	41500	0.129
		80	0.045	0.251	24.4	-	33	72200	0.023
		0	0.045	0.250	33.2	-	40	98200	0.007

*Maximum deflection, 118° bend angle, for fixture used.

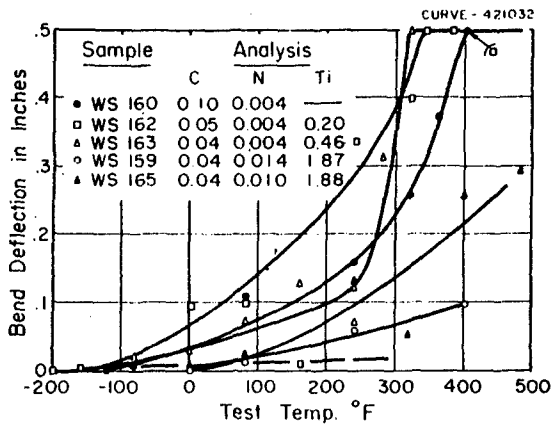


Fig. 16 - Bend Deflection Temp. Relationships for Vacuum Sintered Deoxidized Molybdenum.

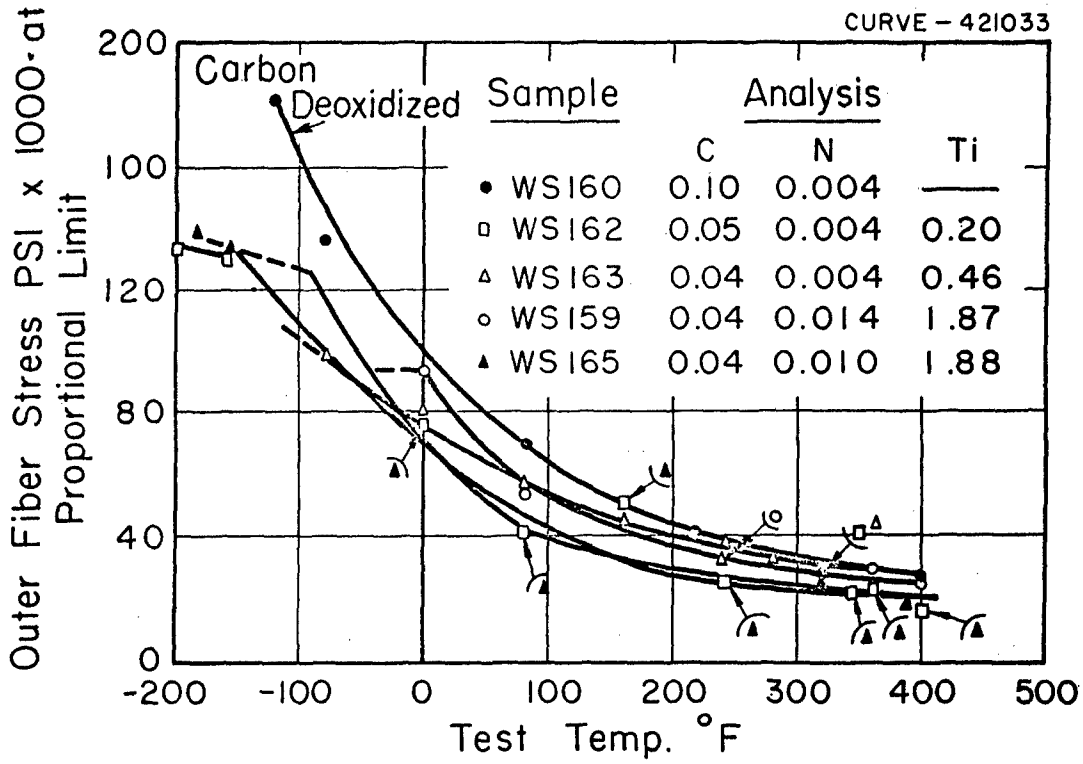


Fig. 17 - Stress at Proportional Limit Test Temperature Relationship for Vacuum Sintered Deoxidized Molybdenum.

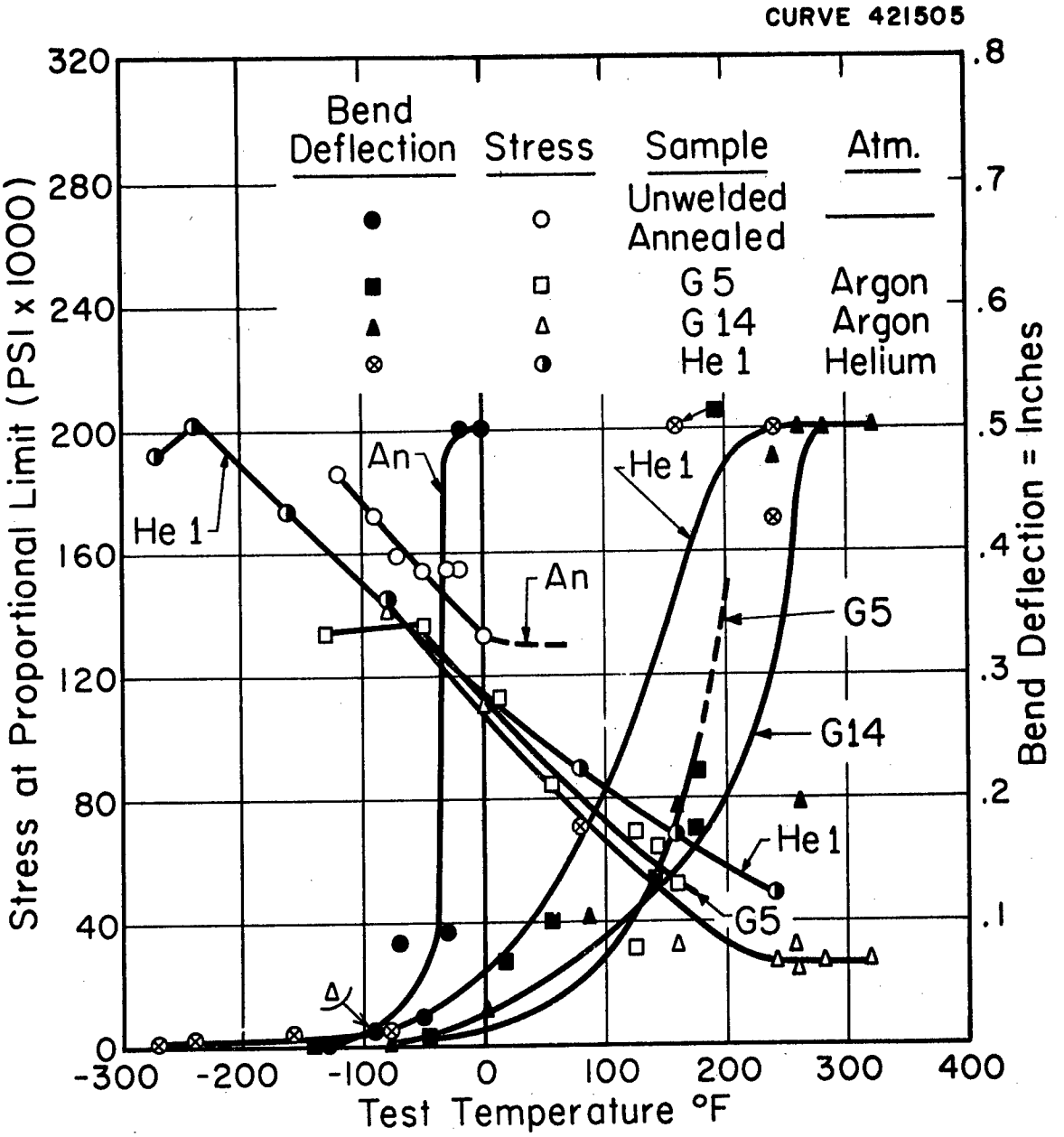


Fig. 18 - Bend Deflection and Proportional Limit as a Function of Test Temperature for Welds in High Purity Atmospheres.

did not attain the same maximum stress at the proportional limit as the carbon deoxidized material. However, the lower temperature for the rise in the proportional limit permits the material to show better bend properties at lower temperatures than the carbon deoxidized material. It is possible that the maximum stress at the proportional limit could be increased by changes in the deoxidizing technique so that more uniform deoxidization could be obtained. The lack of uniformity of deoxidization is suggested by the segregation seen in the photomicrograph of the vacuum sintered titanium deoxidized molybdenum, Fig. 15. Scatter in the bend ductility data also indicates local incomplete deoxidization as shown by the dotted curve for the 0.2% Ti sample, Fig. 16.

A further examination of Fig. 16 shows that the welds in material deoxidized with 0.2 and 0.46% titanium showed the best bend ductility. The samples deoxidized with 1.88% titanium were not completely ductile at temperatures below 400°F. From these data it appears that vacuum sintered molybdenum deoxidized with 0.2% to 0.5% titanium shows weld properties comparable to the welds obtained in arc-cast carbon deoxidized material. However, part of the improved properties of the sintered material may be due to the type of deoxidizer used.

In the search for titanium deoxidized vacuum sintered molybdenum which had improved welding properties, two heats were obtained from the Westinghouse Research Laboratories which had been prepared in a slightly different manner with regard to the deoxidization practice. The titanium powder had been dried prior to mixing so that the segregation of titanium found in the earlier samples would be eliminated. The sintering data for these samples are given in Table V. The photomicrographs of these sintered compacts show nothing unusual when compared with other titanium deoxidized samples. The samples contained 0.1 and 0.2% titanium and from the earlier work should have shown good welding properties. However, a large amount of porosity was observed in both samples after welding. The welding data are shown in Table VI. A photograph and X-ray picture of one of these weld beads reveal porosity, Fig. 19. Characteristic photomicrographs of these welds indicated that the deoxidization practice used in sintered molybdenum is critical if the material is to be welded, Fig. 20. To check the deoxidizing practice, four selected heats were obtained which had been titanium deoxidized using different methods of powder addition. One sample had been made with the titanium powder added as-received

TABLE V

VACUUM SINTERING DATA FOR TITANIUM DEOXIDIZED MOLYBDENUM

Sample	Composition Aim	Sintering Time	Sintering Temp. °C	As Sintered Hardness	As Sintered Density
WS195	0.1% Ti	4	2000	151	9.86
WS196	0.2% Ti	4	2000	156	9.93

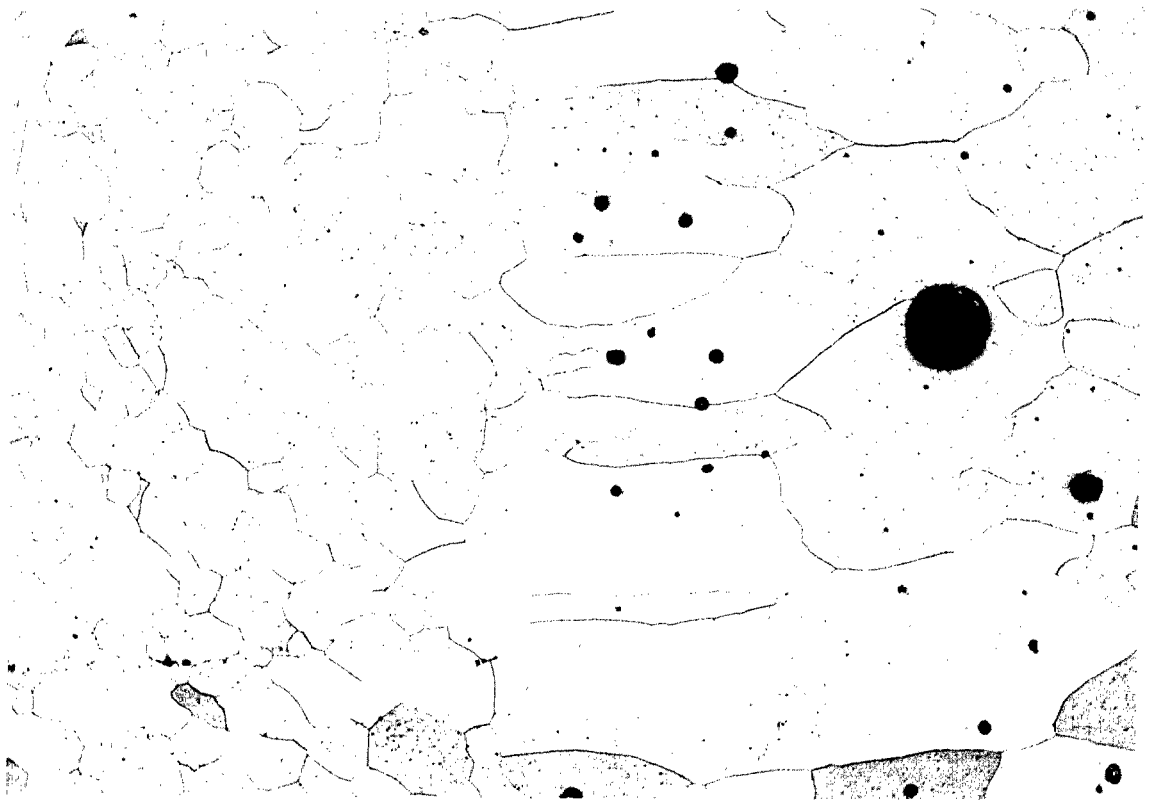
TABLE VI

WELDING DATA Ti DEOXIDIZED VACUUM SINTERED MOLYBDENUM

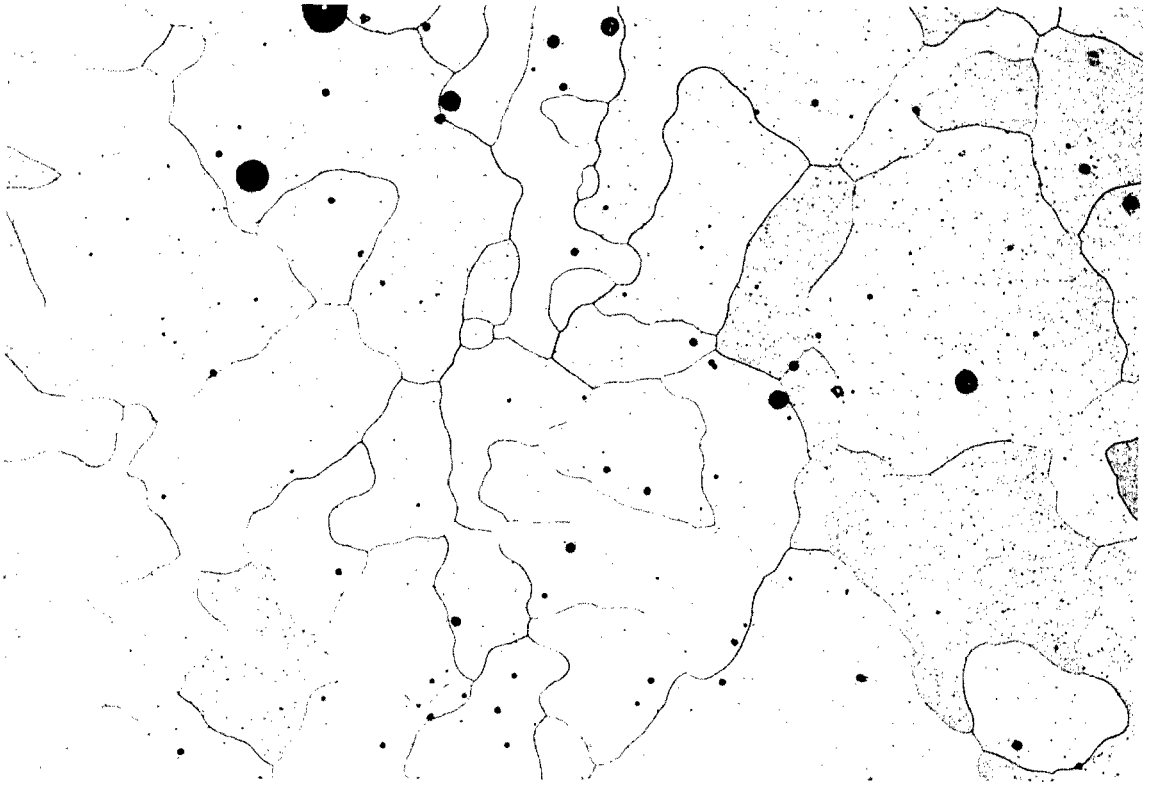
Sample	Analysis	Atmosphere	Current Amp	Voltage Volts	Arc Travel Speed	Comments
WS195	0.1% Ti	N_2 0.02% O_2 0.02%	168	13	6 in./min	Clean, bright, no cracks, porous
WS196	0.2% Ti	N_2 0.02% O_2 0.02%	170	13	6 in./min	Clean, bright, no cracks, porous

R 13082

Fig. 19 - Weld in 0.2% Ti Deoxidized Vacuum Sintered Mo. WS 195

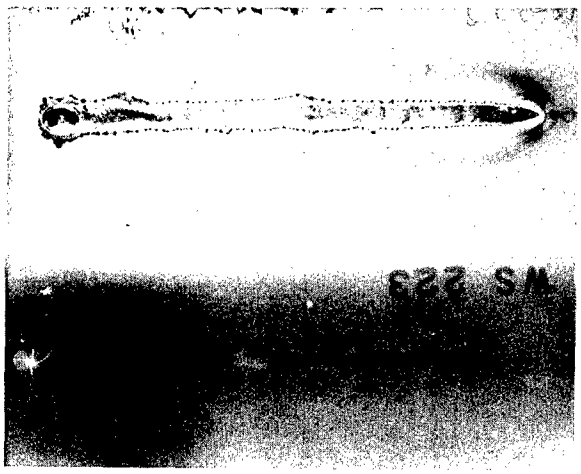


(a) Edge of Weld P54-97-16



(b) Center of Weld P54-97-17

Fig. 20 - Weld in 0.2% Titanium Deoxidized Vacuum Sintered Molybdenum. WS196 100X

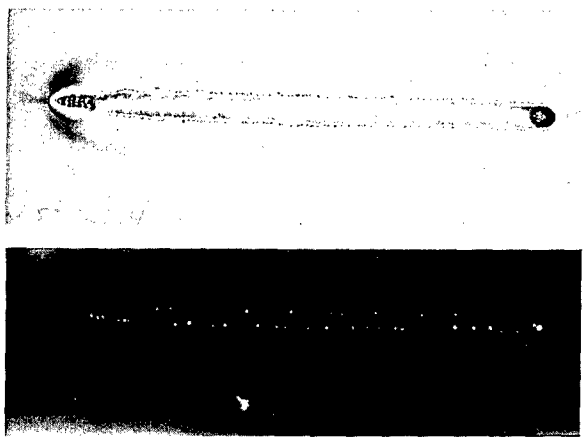


R 13192

(a) Ti Powder Added Wet. WS223

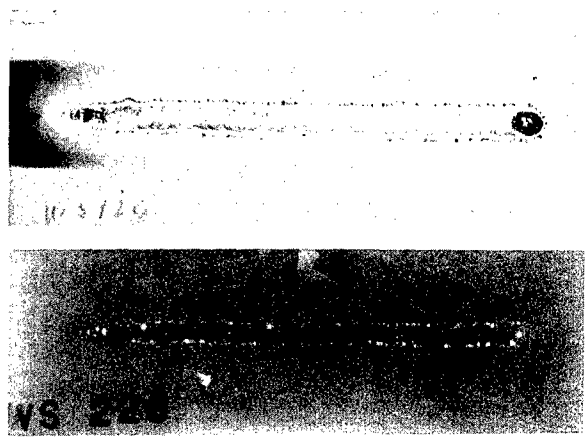
R 13191

(c) Ti Powder Washed in Acetone and Vacuum Dried. WS225



R 13189

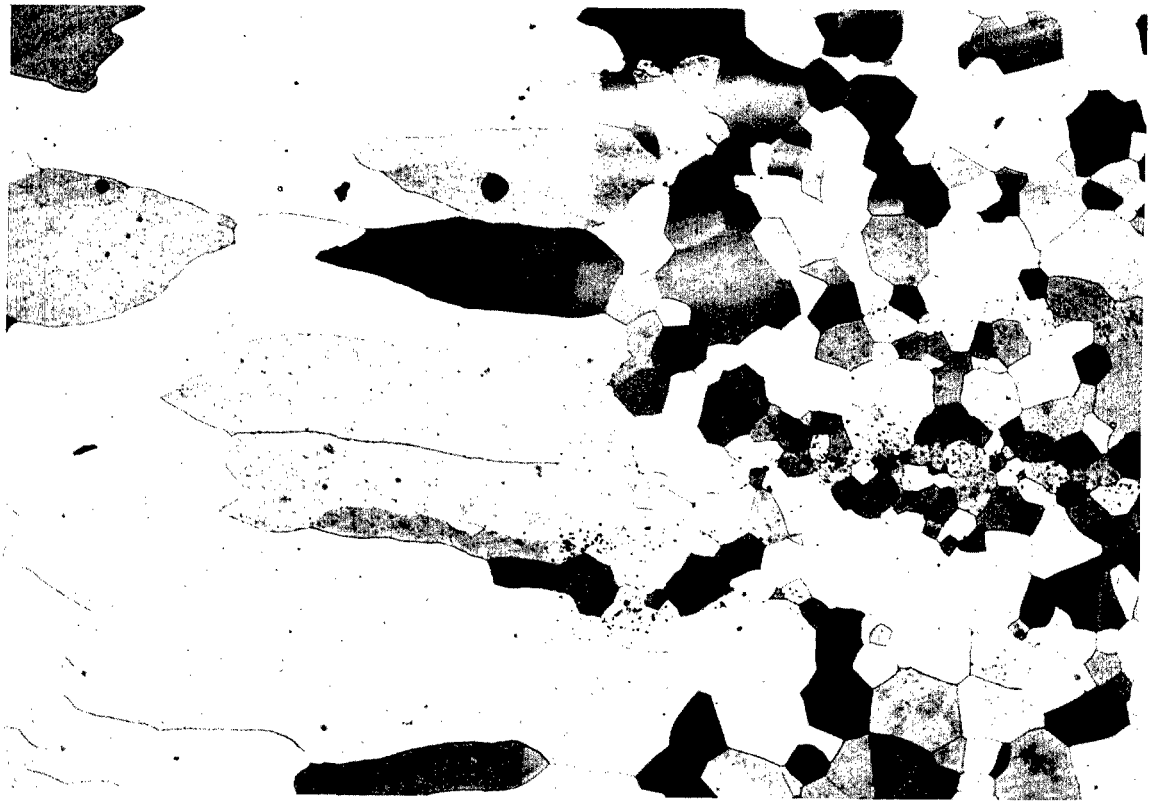
(b) Ti Powder Vacuum Dried 115°C. WS224



R 13190

(d) Ti Powder Vacuum Dried. WS226

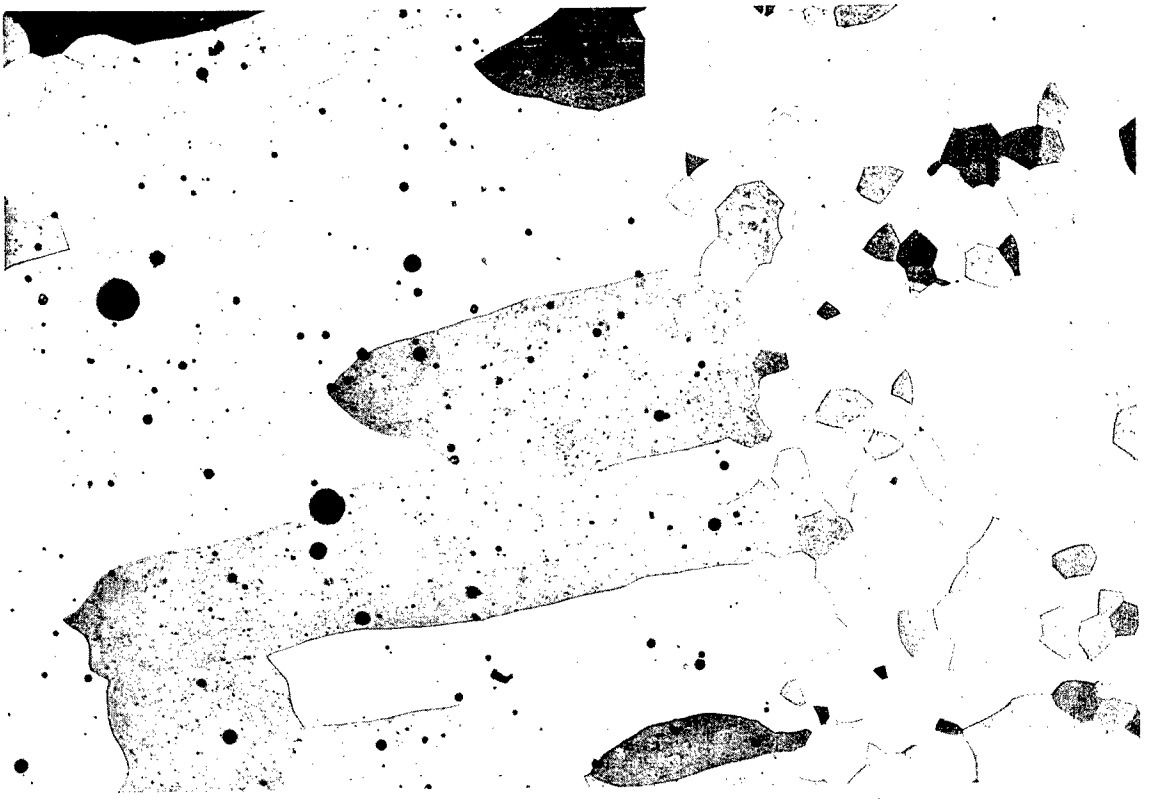
Fig. 21 - Welds in 0.2% Titanium Deoxidized Sintered Molybdenum Made Using Various Deoxidization Methods.



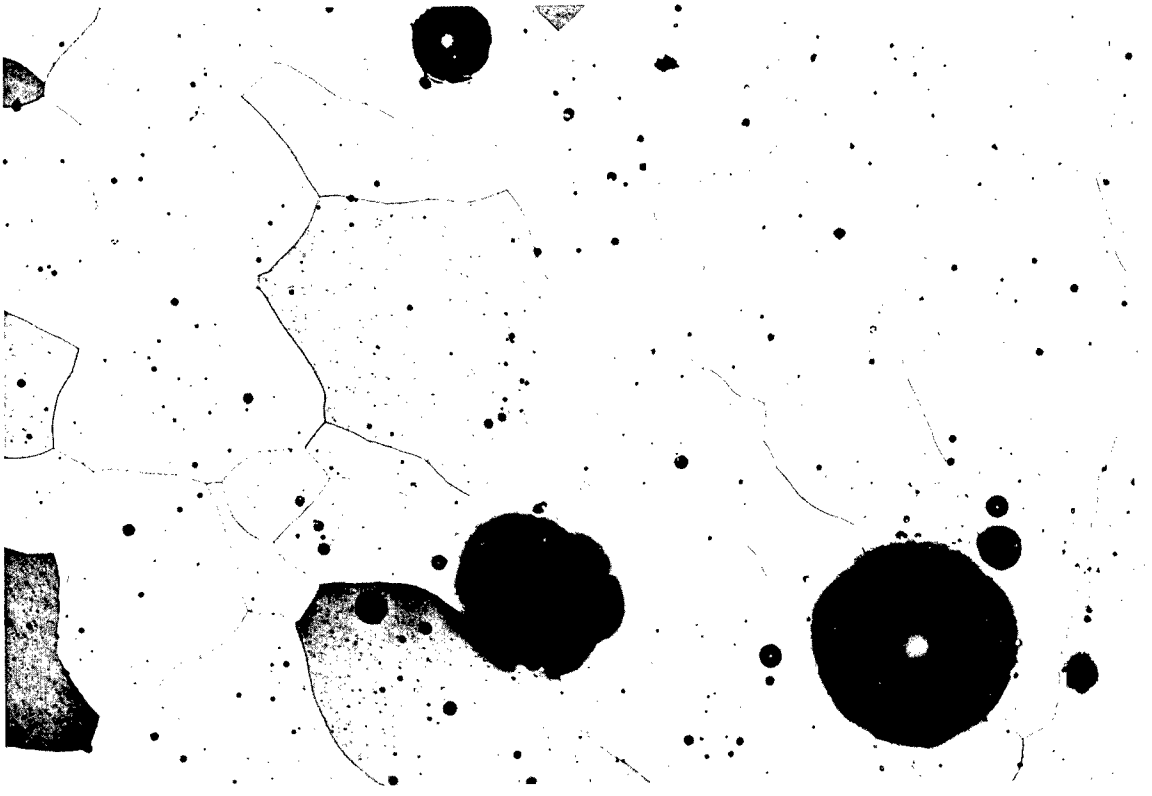
(a) Ti Powder Added Wet. 100X

(b) Ti Powder Vacuum Dried at 115°C 100X

Fig. 22 - Welds in 0.2% Ti Deoxidized Molybdenum. Deoxidized in Various Ways. P54-144-3,1,5,6. (Continued)



(c) Ti Powder Washed in Acetone and Vacuum Dried. 100X



(d) Ti Powder Vacuum Dried 100X

Fig. 22 - Welds in 0.2% Ti Deoxidized Molybdenum. Deoxidized in Various Ways. P54-144-3,1,5,6.

with a 20% water content; a second sample had been made with the titanium powder vacuum dried at 115°C; in a third sample the titanium was vacuum dried at room temperature and a fourth sample was made with the titanium powder washed in acetone and vacuum dried prior to mixing. The sintering data are given in Table VII. No detectable difference in structure was found in the as-sintered condition. Weld beads were made on these samples in the welding chamber and the data are shown in Table VIII. Photographs and X-ray pictures of these weld beads, Fig. 21, and photomicrographs, Fig. 22, revealed porosity in all the samples except sample WS223 which was deoxidized with wet titanium powder. In each case where the titanium powder was dried there is evidence of gross porosity in the weld area. Sample WS225, Fig. 21c, showed a crack extending into the bead from the crater. The quality of the weld beads seems to decrease as the drying procedure is improved. These data suggest that the water on the titanium powder acts as a protective coating until the powder is in the vacuum sintering furnace. When the furnace is pumped down to 10^{-5} mm of Hg the water is removed. From these data it is apparent that the method of adding the deoxidizer to the molybdenum powder may be as important as the deoxidizer used. In the case of titanium the powder requires protection whenever exposure to air is likely.

The weld bead in sample WS223, deoxidized with 0.2% wet titanium powder was cut into bend specimens and tested over a range of temperatures. Test data are given in Table IX and Fig. 23. Comparing these data with those shown in Figs. 16-18, it will be seen that the welds in the vacuum sintered molybdenum are comparable to those obtained in arc-cast carbon deoxidized molybdenum. The bend deflection curve shows that the weld had slightly better properties than those found in earlier welds in vacuum sintered material deoxidized with wet titanium powder. This improvement may be due to experimental scatter or improvement in deoxidization practice.

Titanium as a deoxidizer for vacuum sintered molybdenum is most successful in the range 0.2% to 0.5% and the addition of the deoxidizing powder must be carefully made. The powder used for deoxidization must be protected until exposure to air is no longer possible. Adding the titanium powder wet with a 20% water content appears to provide sufficient protection prior to vacuum sintering to provide a product which has satisfactory welding properties.

TABLE VII

DEOXIDIZING AND SINTERING DATA, TITANIUM DEOXIDIZED MOLYBDENUM

Sample	Composition Aim	Sintering Time	Sintering °F Temp.	Hardness DPH	Density gm/cc	Ti Addition Treatment
WS223	0.2%	4	3632	150	9.96	Ti powder added wet, 20% H_2O.
WS224	0.2%	4	3632	153	9.98	Ti powder vacuum dried at 115°C.
WS225	0.2%	4	3632	146	9.83	Ti powder washed with acetone and vacuum dried.
WS226	0.2%	4	3632	149	9.83	Ti powder vacuum dried.

TABLE VIII

WELDING DATA FOR VACUUM SINTERED MOLYBDENUM 0.2% TITANIUM MADE WITH SELECTED DEOXIDIZATION PRACTICES

Sample	Atmosphere Argon Plus	Current Amp	Voltage Volts	Arc Travel Speed In./Min	Comments
WS223	N_2 0.08% O_2 < 0.02%	180	13	6	Crater crack, irregular bead, Ti_2O_3 specks on surface.
WS224	N_2 0.08% O_2 < 0.02%	180	13.3	6	Very porous at start of bead. Some general porosity. No cracks. Ti_2O_3.
WS225	N_2 0.1% O_2 < 0.02%	182	14	6	Slight porosity, center bead crack 1-1/4 in. long, crater crack, Ti_2O_3 specks.
WS226	N_2 0.1% O_2 < 0.02%	182	13.3	6	Porosity along edge of bead, Ti_2O_3 specks, no cracks.

TABLE IX

BEND TEST DATA FOR WELD IN VACUUM SINTERED MOLYBDENUM DEOXIDIZED WITH 0.2% WET Ti POWDER

Sample	Test Temp. °F	Thickness Inches	Width In.	Load at Proportional Limit-Lb	Load at Fracture Lb	Stress at Proportional Limit, psi	Bend Deflection In.
WS223	240	0.044	0.250	8	No Fracture	24,800	0.5
	160	0.044	0.250	9.5	26	29,400	0.107
	80	0.044	0.250	20	33	62,000	0.081
	-40	0.044	0.250	35	48	108,500	0.018
	-60	0.044	0.251	36.5	41	113,000	0.014
	-80	0.045	0.251	-	36	111,500	0.000

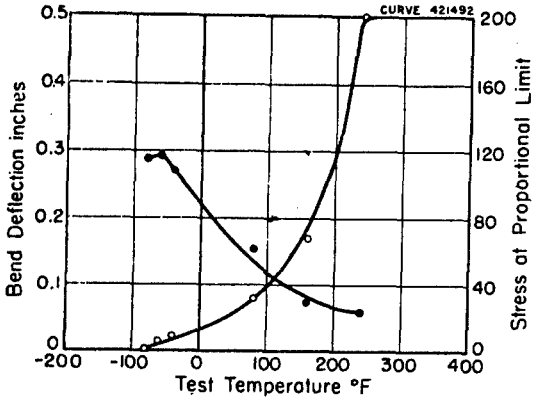


Fig. 23 - Bend Test Results for Weld in Vacuum Sintered Mo Deoxidized With 0.2% Wet Titanium Powder

Carbon Deoxidized Molybdenum

It was first thought that carbon would be a good deoxidizing agent for vacuum sintered molybdenum because the products of deoxidization are volatile and would be expected to be removed during the vacuum sintering process. Exploratory investigations[5] indicated that carbon deoxidized vacuum sintered molybdenum showed some promise as a weldable material. Several heats of carbon deoxidized molybdenum were obtained covering a range of carbon contents to quantitatively determine the usefulness of carbon as a deoxidizer.

Sintering data are given in Table X for the six heats of carbon deoxidized molybdenum used in these investigations. Carbon was added over the range 0.01 to 0.1%. Carbon at 0.01% was found in material to which no carbon additions had been made. This material was used as a control for data collected on vacuum sintered molybdenum. All the sintered molybdenum samples used in this portion of the investigation were mixed according to the procedure discussed under Materials earlier in this report. Sintering was done in vacuum at 10^{-5} mm of Hg between 1950 and 2100°C. The sintering time was four hours. Sintered compacts from the early heats, WS160, WS161, WS164, were porous and photomicrographs were not taken. Only sample WS160, Table X, was sufficiently sound to roll. The two attempts to make carbon deoxidized material containing 0.2% C produced compacts which could not be rolled so no further effort was made in this direction. Two samples were obtained with 0.05% and 0.1% C which were not porous after sintering, WS173 and WS176. These samples were used as a recheck on the results obtained from the porous compact with 0.1% C.

Weld beads were made in the carbon deoxidized heats in the welding chamber using an atmosphere of welding grade argon. Welding data are presented in Table XI. Two samples were made on heat WS160, one in the as-rolled condition and one after the material had been annealed one hour at

TABLE X

SINTERING DATA FOR CARBON DEOXIDIZED MOLYBDENUM

Sample	Intended Composition	Chemical Analysis	Sintering Atmosphere	Sintering Time	Temp. °C	DPH Hardness	Density gm/cc
WS158	Pure Mo	N 0.004 C 0.01	Vacuum 10^{-5} mm Hg	4 hr	2100	136	9.67
WS173	0.05% C	-	"	"	1950	147	9.62
WS160	0.1% C	N 0.004 C 0.10	"	"	2100	Porous	-
WS176	0.10% C	-	"	"	1950	149	9.62
WS161	0.2% C	-	"	"	2050	Porous	-
WS164	0.2% C	-	"	"	2000	Porous	-

TABLE XI

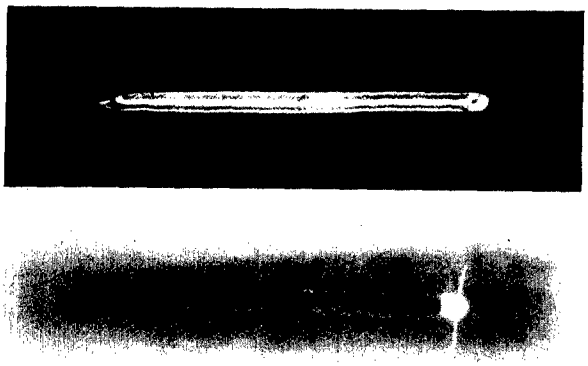
WELDING DATA

C DEOXIDIZED VACUUM SINTERED MOLYBDENUM

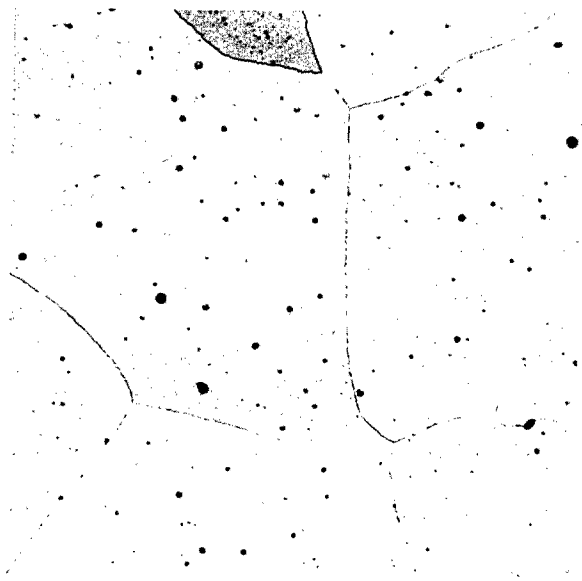
Sample	Composition Aim	Atmosphere	Current Amp	Voltage	Speed In./Min	Comments
WS160	0.1% C, Bal. Mo	99.9% A 0.1% N_2	180	14	6	Clean, bright, with crater crack.
WS160A	0.1% C, Bal. Mo, Annealed 1 hr 1200°C	99.9% A 0.1% N_2	180	13	6	Bright, clean, medium width bead. No cracks.
WS173	0.05% C	<.05 Impurity	208	14	6.2	Trouble starting arc. Gas evolution in bead. No crack. Edge porosity.
WS176	0.1% C	<.05 Impurity	205	13.3	6.2	Clean, bright, rough bead, no cracks. Edge porosity.

1200°C. A photograph of one of these welds is shown in Fig. 24. The X-ray pictures show no evidence of porosity. A crater crack was found in the unannealed sample, however, this type of crack has been found to occur in a random fashion when the weld is terminated on the plate. Crater cracks are probably due to the stresses in the plate resulting from the type of bead on plate specimen used. Mark[11] has shown that stresses exist in the direction of the weld bead in this type specimen. The reduced section at the weld crater and the residual stresses would account for the crater cracking. It will be shown later that oxygen in the welding atmosphere over 0.02% will also cause crater cracking.

The improvement due to deoxidization is evident if the weld shown in Fig. 24 is compared with a weld made in a sample which was not deoxidized, Fig. 12, WS158. A gross center bead crack occurs when deoxidization is not accomplished. A photomicrograph of the weld area is shown in Fig. 25 and should be compared with the control sample, Fig. 14, where grain boundary cracking occurred. Gross porosity also occurred in the sample without deoxidizer additions. Center bead cracks are absent in the carbon deoxidized sample but there is some evidence of fine porosity. The bend ductility of sample WS160, 0.1% C, was shown earlier in Figs. 16 and 17. This material was ductile in the bend test, that is, it withstood 118° bend at 400°F and did not become completely brittle until -130°F. The properties were not as good as those obtained with Ti deoxidized molybdenum. The carbon



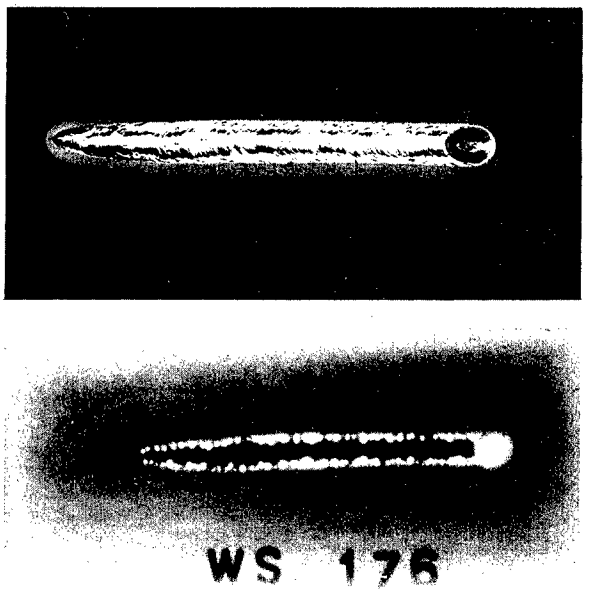
R 12589
Fig. 24-Weld in Vacuum Sintered Mo, 0.1% C. Welding Atmosphere Argon. WS160



P53-215-22
Fig. 25.-Welds in 0.1% C Deoxidized Molybdenum. WS160. 300X

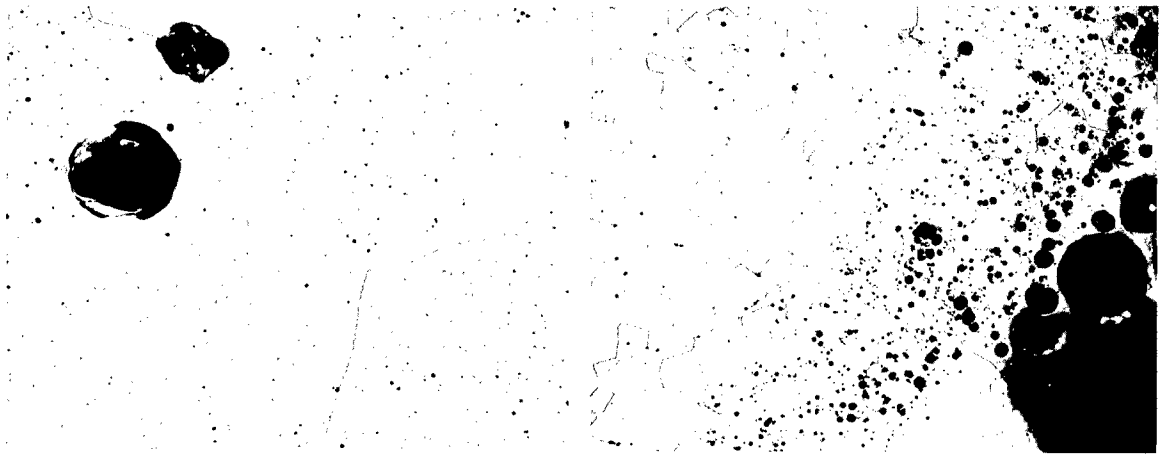
R 12947

Fig. 26 - Weld Bead in Vacuum Sintered Molybdenum Deoxidized With 0.05% C, WS173.



R 12948

Fig. 27 - Weld Bead in Vacuum Sintered Molybdenum Deoxidized with 0.1% C, WS176.



P54-47-5, 100X
(a) Center of Bead

P54-47-4, 100X
(b) Edge of Bead

Fig. 28 - Weld Bead in Carbon Deoxidized Molybdenum. Vacuum Sintered.

deoxidized material also shows the rise in the elastic limit, with decreasing temperature at higher temperatures than the Ti deoxidized material.

The welding results obtained with the first lot of carbon deoxidized vacuum sintered molybdenum could not be duplicated. Two heats were tried,

one with 0.05% C and one with 0.1% C. Photographs of these welds are shown in Figs. 26 and 27. The welds showed no cracks after welding. Sample WS173 was damaged after welding and cracked at that time. Both welds showed gross porosity at the edge of the weld bead, Figs. 26 and 27. This porosity is shown in the photomicrographs of the weld area, Fig. 28.

Removal of the products of deoxidization by formation of a volatile deoxidization product was mentioned as being one of the advantages in using carbon. Unfortunately, this characteristic does not operate where welding applications are involved. Deoxidization does not appear to be completed during the sintering process. Completion of the deoxidizing action during welding and the production of gaseous products of deoxidization produce porosity in the weld bead. Porosity at the edge of the weld bead indicates the occurrence of deoxidization during welding and the absence of hot center bead cracking shows that deoxidization was reasonably complete after welding. The data collected in these investigations indicate that carbon is not successful as a deoxidizer in vacuum sintered molybdenum if the material is to be used in welding applications.

Aluminum Deoxidized Molybdenum

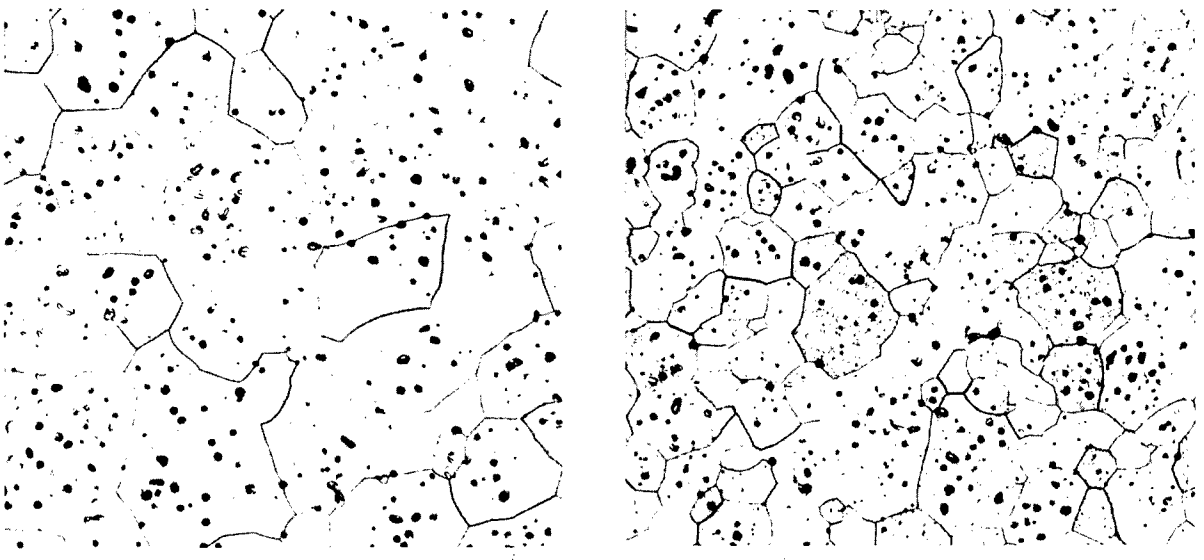
Exploratory investigations[5] indicated that aluminum could be used as a deoxidizer for molybdenum. The product of the deoxidization reactions would be reasonably stable at elevated temperatures and should not cause difficulty in welded applications. Unfortunately, one very important factor was overlooked in the selection of aluminum for deoxidization reactions in sintered molybdenum for welding. Aluminum boils at 2450°C which is well below the melting point of molybdenum and above the sintering temperature used. The welding data shown in this report demonstrate the effect of deoxidizers which boil at or below the melting point of the metal deoxidized.

Six heats of aluminum deoxidized vacuum sintered molybdenum were obtained in the range of 0% to 0.2% Al. These samples were made up from freshly reduced molybdenum powder and sintered four hours at 1950 to 2000°C. The sintering process would not have removed the excess aluminum. Sintering data for the aluminum deoxidized heats are given in Table XII. Typical photomicrographs are given in Fig. 29 which show aluminum deoxidized material and material without deoxidizing additions.

TABLE XII

VACUUM SINTERING DATA FOR ALUMINUM DEOXIDIZED MOLYBDENUM SAMPLES WS189-193

Sample	Deoxidizer Addition	Sintering Time	Sintering Temp.°C	DPH Hardness	Density gm/cc
WS194	0	4 hr	2100	145	9.85
WS189	0.05% Al	4	2100	150	10.01
WS172	0.1% Al	4	1950	149	9.85
WS188	0.1% Al	4	2000	147	9.85
WS193	0.2% Al	4	1950	149	9.79
WS177	0.2% Al	4	1950	154	9.81



P54-84-6 - 200X

(a) No Deoxidation, WS194

200X - P54-84-3

(b) 0.2% Al, WS177

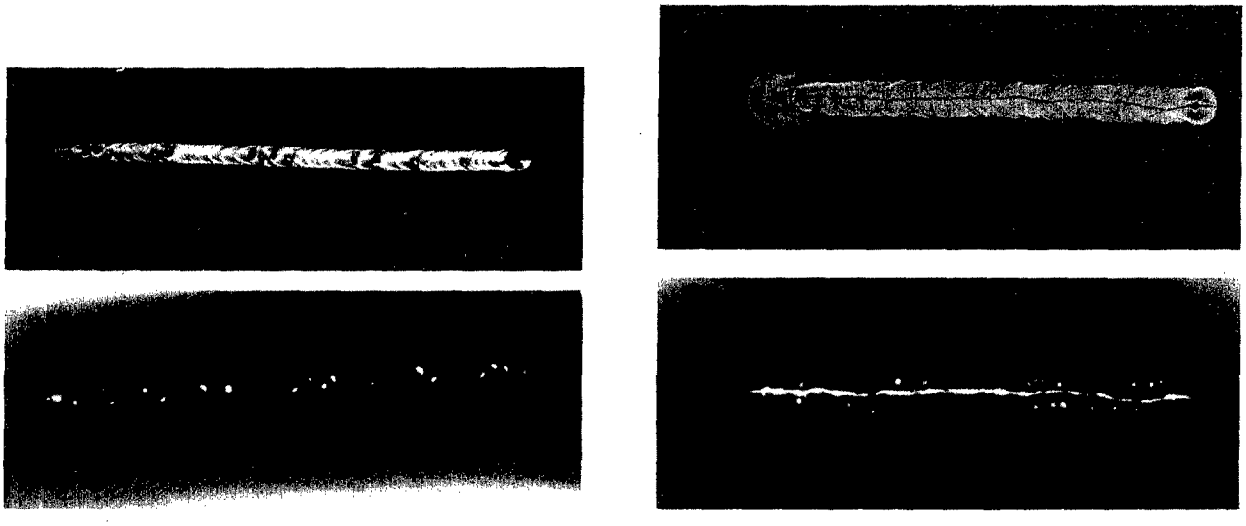
Fig. 29 - Vacuum Sintered Molybdenum With and Without Aluminum Deoxidizer Addition.

Weld beads were made on aluminum deoxidized molybdenum samples in the welding chamber using a welding grade argon atmosphere. The welding data are given in Table XIII. All of these welds showed porosity and all but one showed center bead cracking. The photographs and X-ray pictures of typical welds in aluminum deoxidized molybdenum, Fig. 30, demonstrate the location of the porosity and cracking. A series of typical photomicrographs are shown in Fig. 31.

TABLE XIII

WELDING DATA FOR VACUUM SINTERED ALUMINUM DEOXIDIZED MOLYBDENUM

Sample	Deoxidizer	Atmosphere	Current Amp	Voltage	Arc Travel Speed In./Min	Comments
WS189	0.05% Al	N_2 0.02% O_2 0.02%	175	12.5	6	Very porous, center bead crack.
WS188	0.1% Al	N_2 0.02% O_2 0.02%	180	13	6	Very porous, crack down center.
WS177	0.2% Al	N_2 0.02% O_2 0.05%	203	13.5	6	Rough bead surface, center bead crack. Edge porosity.
WS193	0.2% Al	N_2 0.06% O_2 0.02%	175	13.5	6	Oxides on bead, rough bead, very porous.
WS194	None	N_2 0.06% O_2 0.02%	180	13	6	Center bead crack.



R13081

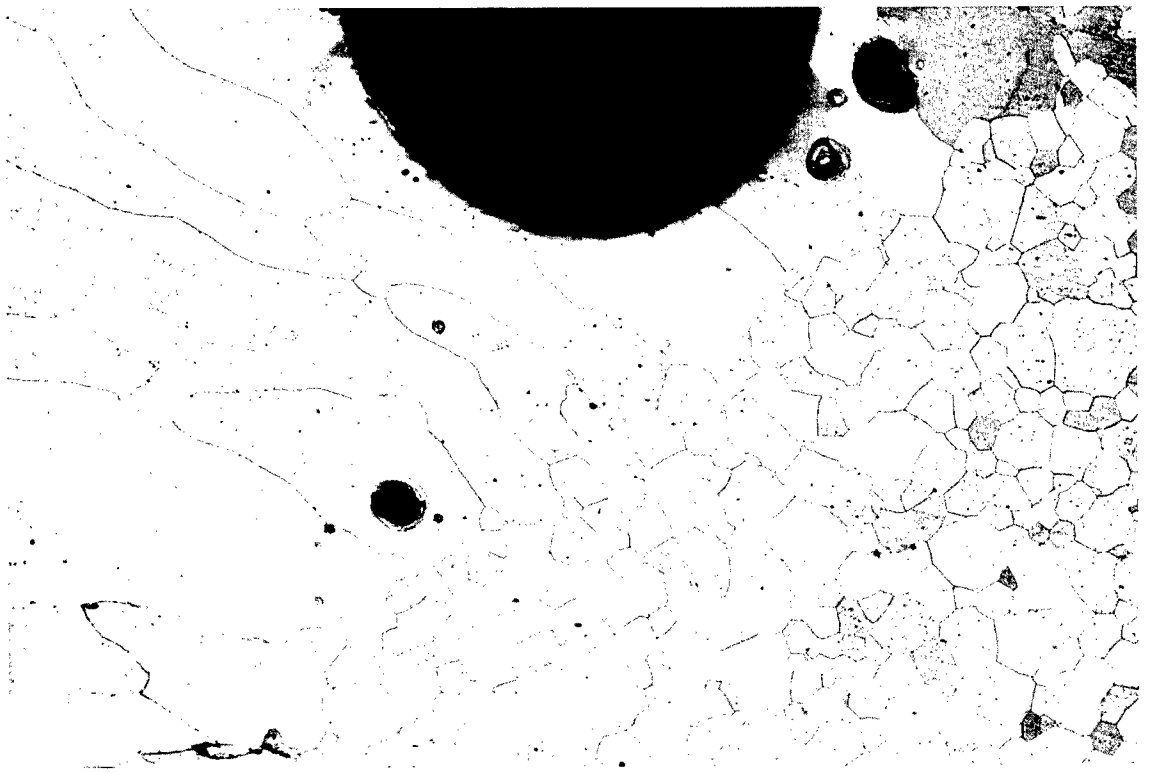
(a) WS193

R12945

(b) WS177

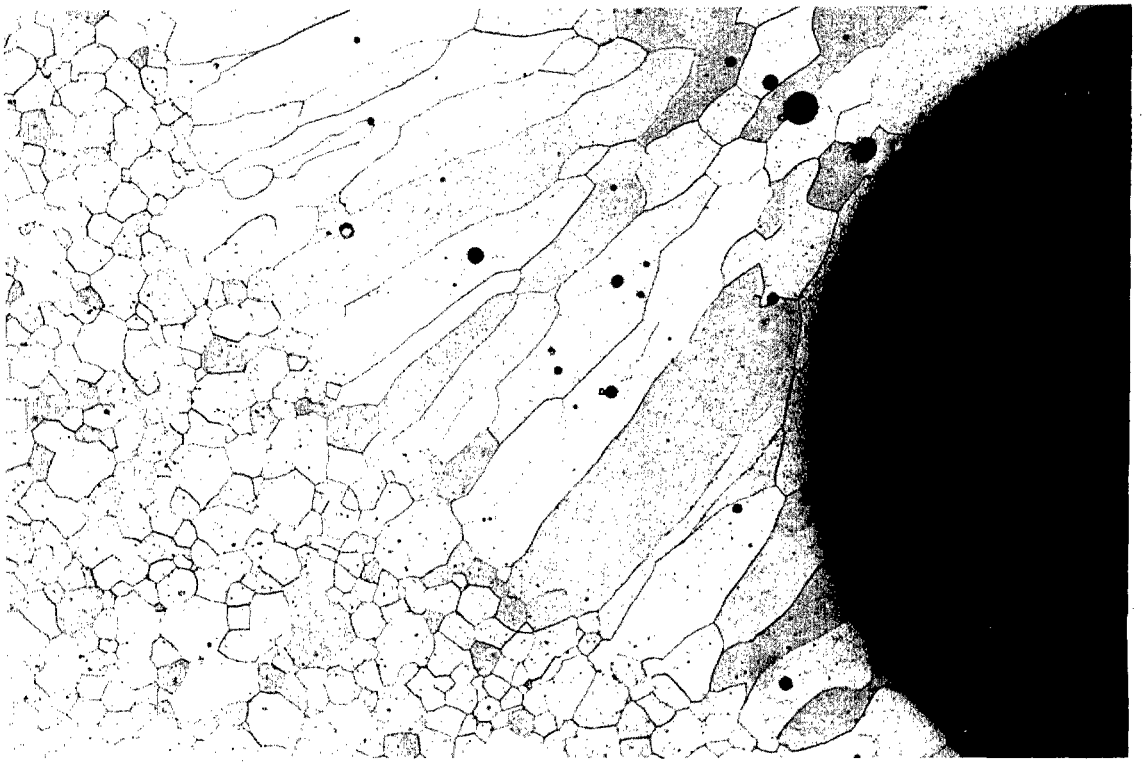
Fig. 30 - Welds in 0.2% Aluminum Deoxidized Vacuum Sintered Molybdenum.

(a) 0.5% Al, WS189 100X P54-97-9

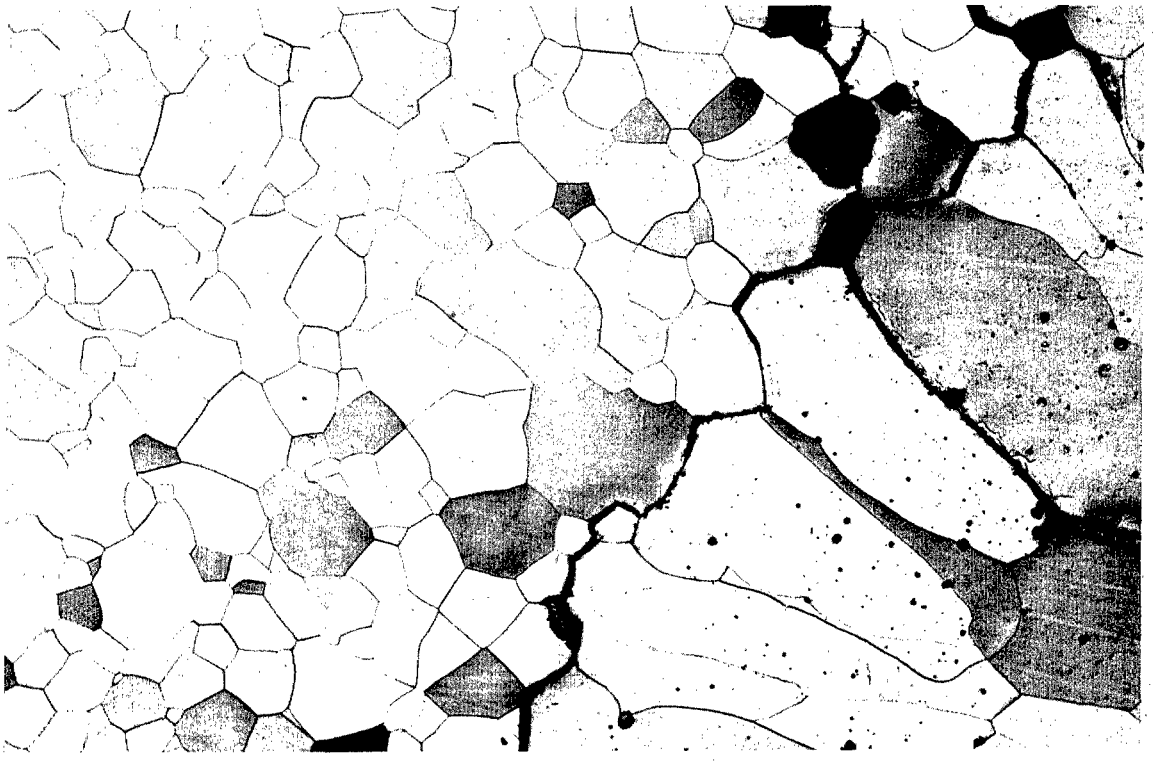


(b) 0.1% Al, WS188 100X P54-47-1

Fig. 31 - Welds in Aluminum Deoxidized Vacuum Sintered Molybdenum. (Continued)



(c) 0.2% Al, WS193 100X P54-97-10



(d) No Deoxidizer, WS194 100X P54-97-12

Fig. 31 - Welds in Aluminum Deoxidized Vacuum Sintered Molybdenum. (Continued)

(e) No Deoxidizer, WS194 100X P54-97-13

Fig. 31 - Welds in Aluminum Deoxidized Vacuum Sintered Molybdenum.

The boiling action of the aluminum is evident and it appears that some form of grain boundary eutectic may exist after the molybdenum has solidified so that boundary cracking occurs during cooling. The aluminum oxide melts at 2015°C[12] and could cause this type of hot grain boundary weakness. However, the same type of failures could have been caused by incomplete deoxidization and the residual molybdenum oxides could cause cracking and porosity during welding. Either one of these reactions would produce material not suitable for welding applications.

From these data it is obvious that aluminum is not successful as a deoxidizer for vacuum sintered molybdenum which is to be used in welding applications. It is also apparent that deoxidizing materials which boil below the melting point of molybdenum will be unsuccessful unless all of the deoxidizer is removed during sintering and the deoxidization is also completed during that time. Materials which form low melting point oxides or oxide eutectics or themselves form eutectics will also be unsatisfactory.

Tantalum and Niobium Deoxidized Molybdenum

Tantalum and niobium are both strong oxide-forming materials and the possibility was considered that they might be successful as deoxidizers for vacuum sintered molybdenum. Both of these materials have high boiling temperatures and melting points near that of molybdenum. Tantalum melts at 3027°C and niobium melts at 1950°C as compared to molybdenum which melts at 2620°C. These materials should not be subject to the difficulties encountered with aluminum deoxidized molybdenum.

Two heats of vacuum sintered molybdenum were obtained from the Metallurgical Department of the Westinghouse Research Laboratories, one deoxidized with 0.2% Nb and the other with 0.2% Ta. The sintering data for these heats are shown in Table XIV. Photomicrographs of the as-sintered

TABLE XIV

SINTERING DATA Ta AND Nb DEOXIDIZED HEATS

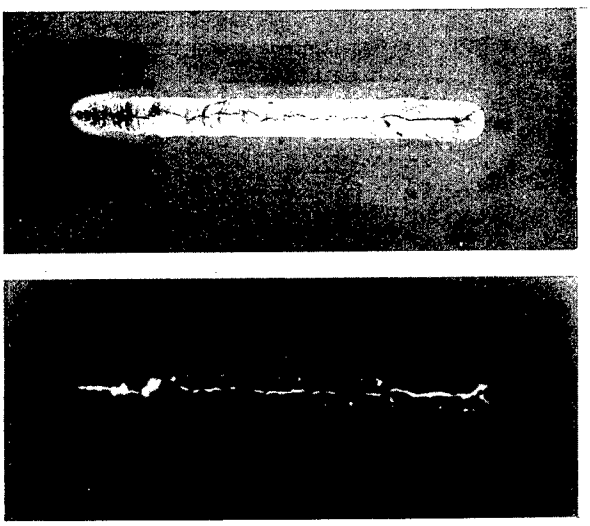
Sample No.	Intended Composition	As Sintered Hardness	Density gm/cc	Sintering Time	Sintering Temp.
WS174	0.2% Ta	148	9.73	4 hr	2000
WS175	0.2% Nb	145	9.69	4 hr	2000

material showed no unusual features. Weld beads were made on these samples in the welding chamber under an atmosphere of argon. Welding data and photographs appear in Table XV and Figs. 32 and 33. Photomicrographs of the weld metal and the recrystallized parent metal are presented in Fig. 34. These data indicate that neither Ta nor Nb shows much promise as deoxidizers for vacuum sintered molybdenum for welding applications. The gross cracking and porosity encountered with these materials suggest that the oxides may have decomposed during welding or sintering and the oxygen is then free to form molybdenum oxides which are known to contribute to hot cracking and porosity. The oxide of Ta decomposes at 1470°C.[12] This decomposition could explain the difficulty encountered with this material. The oxides of Nb both melt below 1780°C and could form eutectics with Mo or wet the grain boundaries. A low melting point grain boundary film would account for center bead cracking. However, incomplete deoxidization is more probably the cause of cracking and porosity in this material.

TABLE XV

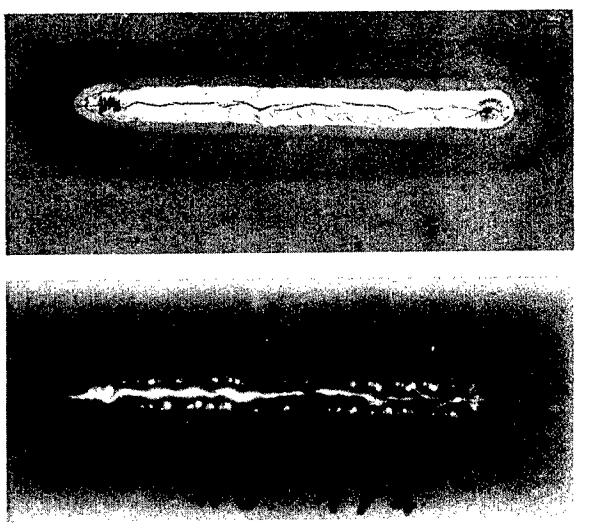
WELDING DATA FOR Ta AND Nb DEOXIDIZED Mo

Sample	Composition Aim	Impurity Content	Current Amp	Arc Voltage	Speed In./Min	Comments
WS174	0.2% Ta	$O_2 < 0.05$	203	13	6	Porous; crack down bead center; crater crack.
WS175	0.2% Nb	$O_2 < 0.05$	203	14	6	Crater crack; center bead crack; gas evolution from bead; general porosity.



R 12946

Fig. 32 - Weld Bead in Vacuum Sintered Molybdenum Deoxidized With 0.2% Nb. (WS175)



R 12944

Fig. 33 - Weld Bead in Vacuum Sintered Molybdenum Deoxidized With 0.2% Ta. (WS174)

P54-47-1

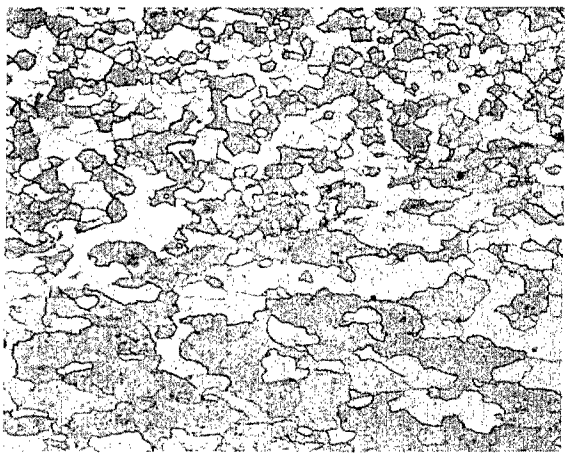
(a) Center of Weld
WS-174 - 0.2% Ta
100X

P54-47-2

(b) Recrystallized Parent Metal
WS-174 - 0.2% Ta
100X

P54-47-9

(c) Center of Weld
WS-175 - 0.2% Nb
100X



P54-47-10

(d) Recrystallized Parent Metal
WS-175 - 0.2% Nb
100X

Fig. 34. Weld Bead and Recrystallized Parent Metal, Niobium, and Tantalum Deoxidized Molybdenum.

Effect of Vacuum Heat Treatment

Samples of hydrogen sintered commercial molybdenum were heated in a vacuum of 10^{-5} mm of Hg for two hours at 800, 1000, and 1300°C in an effort to determine qualitatively if hydrogen and nitrogen would be evolved at the different temperatures and to determine their ultimate effects upon welding with regards to the formation of porosity. The samples were 0.065 in. x 2 in. x 15 in. at the time of heat treatment.

Weld beads were made on these samples in a chamber filled with argon. The welding data and results are given in Table XVI. These tests were inconclusive because the effects of oxygen overshadowed any difficulties resulting from hydrogen or nitrogen.

TABLE XVI

WELDING DATA FOR SINTERED SAMPLES

Sample	Material Analysis	Atmosphere Analysis	Current Amp	Voltage	Arc Travel Speed In./Min	Comments
WS155	100% Mo* Fe 0.045, Ni 0.008	99.9% A 0.1% N_2	185	13	6	Clean, bright, crack full length plus cross cracks.
WS156	100% Mo * Fe 0.005, Ni 0.007	99.9% A 0.1% N_2	180	12-13	6	Cracked full length, porosity.
WS157	100% Mo* Fe 0.008, Ni 0.002	99.9% A 0.1% N_2	185	12-13	6	Bead cracked and porous.
VHT 800	Pure Mo Vacuum* Heat Treated 800°C	99.9% A 0.1% N_2	175	12-13	6	Bright, clean bead, crack full length, cross cracks, porosity.
VHT 1000	Pure Mo Vacuum Heat Treated 1000°C	99.9% A 0.1% N_2	175	12-13	6	Same as VHT800
VHT 1300	Pure Mo Vacuum* Heat Treated 1300°C	99.9% A 0.1% N_2	180	13	6	Same as VHT800

*Commercial Sintered Molybdenum Unalloyed

Effects of Trace Elements

Iron and nickel are frequently found in commercial sintered molybdenum in trace amounts. Since both of these materials may form eutectics with molybdenum and such eutectics would contribute to grain boundary hot cracking, the effects of these elements were investigated with respect to weld quality.

Three heats of commercial sintered molybdenum were selected which had varying Fe and Ni contents. Weld beads were made on these samples in the chamber under argon. Welding and material analysis data are given in Table XVI. In each instance the affects of Fe and Ni were obliterated by the affects of oxygen and the tests were inconclusive.

Summary of Work on Sintered Molybdenum

The work on vacuum sintered molybdenum has shown that if this material is properly deoxidized it can be welded. Welds made in suitably deoxidized molybdenum will be sound and have ductility comparable to welds in carbon deoxidized arc-cast molybdenum. However, there are many restrictions upon the deoxidization practices and materials used in vacuum sintered molybdenum.

If weldable sintered molybdenum is to be obtained the deoxidizer must form nonvolatile products which do not wet the grain boundaries or remain as molten films below the solidification of the molybdenum. The deoxidizer must not become volatile at the temperatures of molten molybdenum. The only material found which meets these requirements is titanium. This deoxidizer forms a nonvolatile product which melts at the temperatures of molten molybdenum but does not form boundary films. Some of the oxides formed when titanium is used are floated off on the surface of the weld bead while the remaining oxides appear as spheres in the bead. Titanium has a limitation in its application in that care must be used to prevent exposure to air prior to sintering. Even relatively short exposure will result in gross porosity in the weld. Protection prior to sintering is relatively simple in the case of titanium. It is necessary to add the material with a 20% water content. The titanium powder is supplied with this amount of water as a safety measure.

Deoxidizing agents tried in these investigations which failed to meet all of the above requirements for deoxidizers failed to produce weldable

sintered molybdenum. Tantalum, niobium, aluminum, and carbon were all found to be unsatisfactory as deoxidizers for sintered molybdenum for welding applications.

V ARC-CAST MOLYBDENUM

Preliminary studies indicated that commercial molybdenum made by the sintering process was not satisfactory for welding. Arc-cast carbon deoxidized molybdenum, however, could be welded with 99.95% pure argon without cracks or porosity. For this reason the arc-cast material was used to determine the effect of contaminating gases in the argon atmosphere upon the weld ductility. The two obvious contaminating gases were oxygen and nitrogen. The works of other investigators[2,3,4,8] had demonstrated that oxygen was a source of difficulty with respect to weld ductility. However, definite welding limitations had not been established. A study of the effect of deliberate controlled oxygen additions to the welding atmosphere was therefore made to determine the effects of oxygen upon the weld quality and ductility. Nitrogen was also studied to determine similar relationships. The combined effects of oxygen and nitrogen were also studied so that their interactions could be quantitatively established.

Welds in Oxygen Bearing Atmospheres

The effects of oxygen upon weld quality and ductility were established by making additions of a 1% oxygen-argon mixture to welding grade argon (99.95%) so that atmospheres were obtained over the range from 0.02% to 0.4% oxygen. The upper limit of 0.4% was established by the formation of hot center bead weld cracks with this amount of oxygen in the welding atmosphere. Further additions would not have added to the information obtained. The lower limit was the best purity obtained from commercial welding grade argon without purification.

Welds were made in the as-rolled plate and in plate annealed for one hour

at 1200°C. Some of the welds in as-rolled plate were shown in the previous annual report.[5] However, test results were not available at that time so that these data are repeated to improve the report continuity. The welding data and results of all welds made in argon-oxygen atmospheres are given in Table XVII. Weld center bead cracking was observed in welds made in atmospheres containing 0.2% to 0.4% oxygen. It was necessary to recheck the as-rolled sheet in welding atmospheres containing 0.05 + 0.2% oxygen. Samples G16, G17, G27, and G28 were used to examine this range. The effect of oxygen upon weld beads made in annealed sheet was also examined, Table XVII. Fourteen weld beads were made using arc-cast carbon deoxidized molybdenum which had been annealed for one hour at 1200°C. The first four of these welds, AG30a-d, were made with less than 0.02% oxygen in the welding atmosphere as a control. Welds were made using 0.05%, 0.08%, and 0.1% oxygen in the argon atmosphere.

It was observed from both surface appearance and the radiographs of the welds described in Table XVII that all types of weld cracking increase grossly with oxygen contents above 0.05%. When oxygen was 0.02% or less in the welding atmosphere, no cracking was observed. These results are similar for annealed or as-worked sheet so that annealing prior to welding does not appear to be beneficial. Two types of hot cracks appear in these samples. Center bead cracks which occur along the longitudinal axis of the weld bead are found in welds made with more than 0.1% oxygen in the welding atmosphere. This type of cracking is possible between 0.1% and 0.2% oxygen, probable between 0.2% and 0.4%, and will always occur with more than 0.4% oxygen in the atmosphere. These data apply when the nitrogen content of the welding atmosphere is 0.1% or less. The effect of nitrogen on weld cracking and ductility will be discussed in another section of this report. Between 0.02 and 0.1% oxygen in the welding atmosphere, crater cracking occurs. Between 0.02% and 0.05% crater cracking is intermittent, but above 0.05% crater cracking is probable in welds where the weld crater occurs in an area surrounded by the plate.

Welds made in carbon deoxidized arc-cast molybdenum under argon-oxygen atmospheres were tested in bending using the test equipment discussed earlier. Specimens from each weld bead were tested over a range of temperatures to determine the effect of test temperature upon the bend ductility. The test

TABLE XVII

WELDING DATA

ARGON-OXYGEN TEST WELDS

Sample	Atmosphere A%	Atmosphere O_2%	Atmosphere N_2%	Welding Current Amp	Welding Voltage	Arc Travel In./Min	Comments
G-1	99.95	-	-	160	13	-	Insufficient melting.
G-1a	99.95	-	-	180	13	6.2	Repeat bead on top of G1. Distortion. Sample rejected.
G-2	Sample bottle leaked. Input gas welding grade argon.			175	13	6.9	Weld bead bright. Sample clean and free from oxide.
G-3	99.95	0.05	Nil	178	13.5	6.9	Welding voltage on before stabilizer. Weld bright and clean.
G-4	Sample bottle leaked air.			180	13	6.5	Weld bright, clean. No oxide on sample or bead.
G-5	99.95	0.05	Nil	185	13	7.1	Sample bright and clean, no oxide.
G-6	99.4	0.4	0.2	170	15	6.9	Sample cracked down center of bead.
G-7	99.6	0.3	0.1	180	14	7.1	Weld cracked at ends of bead.
G-8	99.7	0.2	0.1	175	13.5	6.2	Weld cracked down center of bead.
G-9	99.7	0.2	0.1	175	14	6.9	Small crack at start of bead.
G-10	-	-	-	-	-	-	Speed too high, insufficient melting. Sample rejected.
AG-11*	99.9	Nil	0.1	185	12	5.6	Sample clean, bright, free from cracks. Sample annealed before welding 1200°C one-half hour.
G-12	99.85	0.02	0.13	180	12.7	5.12	Arc flare at start of weld. Weld not cracked.
G-13	99.9	0.05	0.05	180	13	5.05	Crack across crater occurred after sample had been removed and was cold.

*Note: All samples with prefix "A" were annealed 1 hr at 1200°C prior to welding.

TABLE XVII

WELDING DATA

ARGON-OXYGEN TEST WELDS

(Continued)

Sample	Atmosphere A%	Atmosphere O_2%	Atmosphere N_2%	Welding Current Amp	Welding Voltage	Arc Travel In./Min	Comments
G-14	99.97	Nil	0.03	180	13	5.57	Weld not cracked.
G-15	Welded in air. Conventional torch and shielding.			180	-	5.41	Argon flow 5 liters/min, 10.6 cu ft/hr
G-16	99.76	0.18	0.06	170	14	5.73	Weld cracked.
G-17	99.75	0.20	0.05	175	13.5	5.88	Weld cracked.
G-27	Analysis error			180	12.75	5.45	Narrow bead with faint brown oxide deposit, small bead and crater crack.
G-28	Analysis Error			185	12.5	6.4	Faint brown oxide deposit, crack at crater and start of bead.
AG-30a*	99.88	0.02	0.1	185	13	6.20	Clean, bright, no cracks, 90% penetration.
AG-30b	99.88	0.02	0.1	180	13	6.2	Bright, clean, 90% penetration, no cracks.
AG-30c	99.88	0.02	0.1	180	12	6.2	Narrow bead, no cracks, bright, clean.
AG-30d	99.88	0.02	0.1	180	12	6.2	Clean, bright, 95-100% penetration, no cracks.
AG-31b	99.88	0.02	0.1	175	13	6.2	Same as AG-31a.

*Note: All samples with prefix "A" were annealed 1 hour at 1200°C prior to welding.

TABLE XVII

WELDING DATA

ARGON-OXYGEN TEST WELDS

(Continued)

Sample	Atmosphere A%	Atmosphere O_2%	Atmosphere N_2%	Welding Current Amp	Welding Voltage	Arc Travel In./Min	Comments
AG-32a*	99.9	0.05	0.05	175	13	6.2	Arc had trouble starting. Crack near crater. 90-100% penetration.
AG-32b	99.9	0.05	0.05	170	13.5	6.2	Oxides around bead. Crack near crater and at one end.
AG-31a	99.9	0.08	0.02	175	13.5	6.2	Oxides around bead, 90-100% penetration, crater crack.
AG-33a	99.8	0.1	0.1	170-175	13	6.02	Crack down center of first quarter of bead. Crater crack, 100% penetration.
AG-33b	99.8	0.1	0.1	170	14	6.02	Difficulty starting arc. Crater crack and cross bead crack.

*Note: All samples with prefix "A" were annealed 1 hour at 1200°C prior to welding.

data for the argon-oxygen series of welds are given in Table XVIII. These data are shown in the form of temperature deflection curves in Figs. 35-37. The curves demonstrate the effects of oxygen acquired during welding on the ability of molybdenum weld metal to sustain plastic deformation. The most obvious effect is the shift in the temperature for 0.5 in. deflection or 118° angle of bend. Welds made in argon with as little as 0.02% oxygen and 0.1% nitrogen have the temperature of ductile behavior shifted from 0°F in the recrystallized unwelded material to +200°F. A portion of this effect is due to the nitrogen acquired during welding. The effect of nitrogen will be discussed in a later section. Oxygen added to the welding atmosphere will cause the temperature for 0.5 in. deflection to be shifted to higher temperatures. Additions of 0.1% increase the temperature for 0.5 in. bend deflection to 400°F or more. Oxygen additions to the atmosphere of 0.2 to 0.3% increased the 0.5 in. deflection temperature to temperatures above 600°F which was the upper limit of the test fixture. Figs. 35 and 37 show the effect of oxygen on the temperature for 0.5 in. bend deflection.

A second effect occurs as a result of oxygen additions to the welding atmosphere. The temperature of completely brittle failure, fracture without measurable plastic deformation, increases with increased oxygen additions. This effect is shown in Fig. 38. It can be seen that as the oxygen in the welding atmosphere is increased the temperature for completely brittle fracture increases up to 0.1% oxygen. Beyond 0.1% oxygen there is little change in the temperature for brittle failure. Hot center bead cracking frequently occurs when the oxygen in the welding atmosphere is in excess of 0.1% so that studies of the fracture characteristics in this range become impractical.

The relationship is known between the oxygen in the welding atmosphere and the oxygen acquired by the weld metal during welding, Fig. 39. From these data it has been possible to show by means of a cross plot the relationship between the percent oxygen in the weld bead and the temperature of completely brittle behavior in the bend test, Fig. 40. The experimental data are shown in Table XIX. These curves show the relationship between the amount of oxygen in the weld metal and two criteria for weld ductility in the bend test. The dotted curve suggests the possible effect of grain size on the temperature for 0.5 in. deflection. It is apparent from these data that the ductility of the weld metal is closely related to the amount of oxygen acquired by the

TABLE XVIII

BEND TEST RESULTS
OXYGEN SERIES

Specimen No.	% Oxygen In Atmos.	Test Temp. °F	Thickness Inches	Width Inches	Load at Prop.Limit Lb	Max. Load Lb	Load at Fracture Lb	Deflection at Fracture Inches
5143-1-1	-	-120	.060	.250	-	-	111	-
-2		- 20	.060	.250	93	114	-	No Fracture
-3		- 70	.060	.250	95	-	125	.083
-4		- 90	.060	.250	103	-	114	.009
-5		- 50	.060	.250	93	-	107	.020
-6		- 30	.060	.250	94	-	115	.092
-7		- 0	.060	.250	80	107	-	No Fracture
5143-2-1	-	+ 78.8	.060	.250	70	154	-	No Fracture
-2		-120	.060	.250	111	208	-	No Fracture
-3		-220	.060	.250	115	-	199	.007
-4		-170	.060	.250	103	-	218	.037
-5		-145	.059	.250	104	211	-	No Fracture
-6		-195	.059	.250	128	-	185	.005
-7		-150	.059	.250	113	-	197	.022
-8		-160	.059	.250	125	-	206	.040
G-5-1	0.05	+ 56	.063	.250	55.7	82.8	82.8	.0995
-2		+ 14	.063	.250	73.1	102.6	102.6	.0665
-3		- 58	.063	.250	90.0	101.0	101.0	.0054
-4		-130	.063	.250	-	88.0	88.0	-
-5		+158	.063	.250	34.0	73.0	-	No Fracture
-6		+122	.063	.250	45.0	73.5	73.5	.0762
-7		+140	.063	.250	42.0	75.0	75.0	.1290
-8		+171	.063	.250	44.0	71.5	71.0	.2191
G-7-1	0.3	+ 79	.061	.253	-	-	31	-
-2		+500	.061	.248	29	-	44	.025
G-9-1	0.2	+ 79	.060	.250	-	-	43	-
-2		+500	.060	.250	12	-	30	.013
AG-11-1	0.02	+ 79	.062	.250	-	-	-	-
-2		+ 79	.062	.250	46	-	80	.194
-3		+160	.062	.250	43	-	76	.163
-4		0	.061	.250	66	-	109	.100
-5		- 80	.062	.250	-	-	91	-
-6		- 40	.062	.250	66	-	105	.040
-7		+240	.062	.250	37	77	64	.272
-8		+280	.062	.250	16	60	-	No Fracture
G-12-1	0.02	+ 79	.058	.267	40	-	70	.149
-2		0	.058	.267	59	-	79	.048
-3		- 40	.058	.267	62	-	92	.049
-4		- 80	.058	.267	75	-	99	.005
-5		+160	.058	.267	38	63	-	No Fracture

TABLE XVIII

BEND TEST RESULTS
OXYGEN SERIES

(Contd.)

Specimen No.	% Oxygen In Atmos.	Test Temp. °F	Thickness Inches	Width Inches	Load at Prop.Limit Lb	Max. Load Lb	Load at Fracture Lb	Deflection at Fracture Inches
G-12-6	0.02	+120	.058	.267	38	65	63	.228
-7		+140	.058	.267	41	-	-	.110
-8		+ 40	.058	.267	48	-	84	.088
G-13-1	.05	+ 79	.063	.250	50	-	89	.083
-2		+ 79	.063	.250	56	-	81	.042
-3		+155	.063	.250	40	-	77	.225
-4		+200	.063	.250	38	71.5	71	.219
-5		+280	.063	.250	24	65	-	No Fracture
-6		+240	.063	.250	16	63	-	No Fracture
-7		0	.063	.250	-	-	98	-
G-14-1	0.02	+ 82.5	.060	.252	44	-	78	.103
-2		+160	.060	.252	18.5	-	66	.193
-3		+240	.060	.252	15.5	58.5	38	.478
-4		+320	.060	.252	16	54.3	-	No Fracture
-5		+280	.060	.252	15.5	55.9	-	No Fracture
-6		+260	.060	.252	18	-	59	.193
-7		+260	.060	.252	14	53.5	-	No Fracture
-8		0	.060	.252	66.5	-	82.9	.020
-9		- 80	.060	.252	85	-	99	.003
G-15-1	-	+ 79	.056	.250	52	-	73.3	.079
-2		+160	.059	.250	36.5	-	51	.043
-3		+240	.059	.250	27	55	38	.440
-4		+320	.059	.250	9	52.3	-	No Fracture
-5		+280	.059	.250	8	53.5	42	.398
-6		+300	.059	.250	15	-	35.5	.048
-7		+340	.059	.250	18	52	-	No Fracture
-8		0	.059	.250	64	-	87.5	.030
-9		- 80	.059	.250	-	-	52	-
G-27	0.1	+400	.058	.245	11	42.5	-	No Fracture
		+320	.057	.2465	15	46	-	No Fracture
		+240	.0575	.247	17	53	-	No Fracture
		+220	.0575	.247	16.5	-	45	.089
		+200	.0575	.2455	17.5	-	52.5	.189
		+160	.0575	.247	17	-	59	.193
		+ 82.5	.058	.245	40	-	51	.004
		0	.0575	.246	-	-	59	-
G-28	0.1	+480	.060	.248	13	50	-	No Fracture
		+400	.060	.250	16	50	-	No Fracture

TABLE XVIII

BEND TEST RESULTS
OXYGEN SERIES
(Contd.)

Specimen No.	% Oxygen In Atmos.	Test Temp. °F	Thickness Inches	Width Inches	Load at Prop.Limit Lb	Max. Load Lb	Load at Fracture Lb	Deflection at Fracture Inches
G-28	0.1	+320	.060	.2495	15	51.9	-	No Fracture
		+240	.060	.248	17.5	55	-	No Fracture
		+200	.060	.2495	14	60.5	56.5	.312
		+160	.060	.248	19.5	-	54	.057
		+120	.060	.2495	41	-	52.5	.029
		+ 82.5	.060	.248	-	-	52.5	-
AG-30A	0.02	+240	.057	.247	23	50.5	-	No Fracture
		+200	.0575	.248	25	51.5	-	No Fracture
		+180	.057	.248	25	55	51.5	.290
		+160	.057	.249	37	60	59.2	.208
		+ 79	.057	.248	48	-	73	.168
		0	.057	.247	53	-	83	.123
		- 80	.057	.248	74	-	98	.042
AG-30D	0.02	+320	.0505	.250	12	36.3	-	No Fracture
		+280	.051	.250	16	38.3	-	No Fracture
		+260	.050	.2495	17	38.2	-	No Fracture
		+240	.050	.250	21	40.5	39	.279
		+160	.051	.250	25	43.2	42.8	.220
		+ 79	.051	.250	34	-	57.5	.161
		0	.051	.249	51	-	70	.101
		- 80	.051	.2495	58	-	75	.025
		-160	.051	.250	-	-	70	-
AG-31B	0.02	+320	.058	.248	21	47	-	No Fracture
		+280	.058	.247	19	48	-	No Fracture
		+240	.058	.2465	25	52.3	50.8	.257
		+160	.058	.248	37	58	55.5	.253
		+ 79	.058	.246	51	-	76.5	.126
		0	.058	.248	60	-	75	.016
		- 80	.058	.246	-	-	80	-
AG-32A	0.05	+480	.060	.251	15	-	47	.144
		+460	.060	.251	9	-	18*	Cracked
		+440	.061	.247	14	58	-	No Fracture
		+420	.060	.2515	11	-	29.5*	Cracked
		+400	.060	.251	14	-	29.8	.023
		+360	.060	.251	9	-	21.8	.021
		+240	.060	.251	-	-	26.2	-
		+ 81	.060	.251	-	-	41.8	-
AG-32B	0.05	+320	.055	.249	15	44	-	No Fracture
		+280	.055	.2495	18	45.8	-	No Fracture

TABLE XVIII

BEND TEST RESULTS
OXYGEN SERIES

(Contd.)

Specimen No.	% Oxygen In Atmos.	Test Temp. °F	Thickness Inches	Width Inches	Load at Prop. Limit Lb	Max. Load Lb	Load at Fracture Lb	Deflection at Fracture Inches
AG-32B	0.05	+240	.055	.249	25	46	45	.257
		+160	.055	.250	35	-	54	.121
		+ 79	.056	.250	48	-	71	.144
		0	.055	.250	60	-	67.5	.003
AG-31A	0.08	+240	.060	.249	29	54.5	-	No Fracture
		+160	.060	.250	38	63.3	-	No Fracture
		+140	.060	.249	44	-	67.5	.147
		+120	.060	.250	45	-	51	.010
		+ 81	.060	.249	49	-	67	.037
		0	.060	.250	67	-	79	.008
AG-33A	0.1	+400	.061	.250	17.5	49.5	-	No Fracture
		+380	.060	.250	13	-	27.8	.067
		+320	.062	.250	23	-	42.7	.051
		+240	.0605	.249	27	-	38	.017
		+ 79	.061	.250	-	-	58.3	-
AG-33B	0.1	+400	.060	.2515	16	50.5	-	No Fracture
		+400	.060	.2515	15	-	34	.090
		+360**	.060	.2515	3	-	-	-
		+320**	.060	.251	8	-	12	.008
		+320**	.060	.2515	5	-	6.5	.015
		+240	.060	.251	28	-	45.2	.061
		+ 79	.060	.251	-	-	48	-

*Cracked

**Bad Test

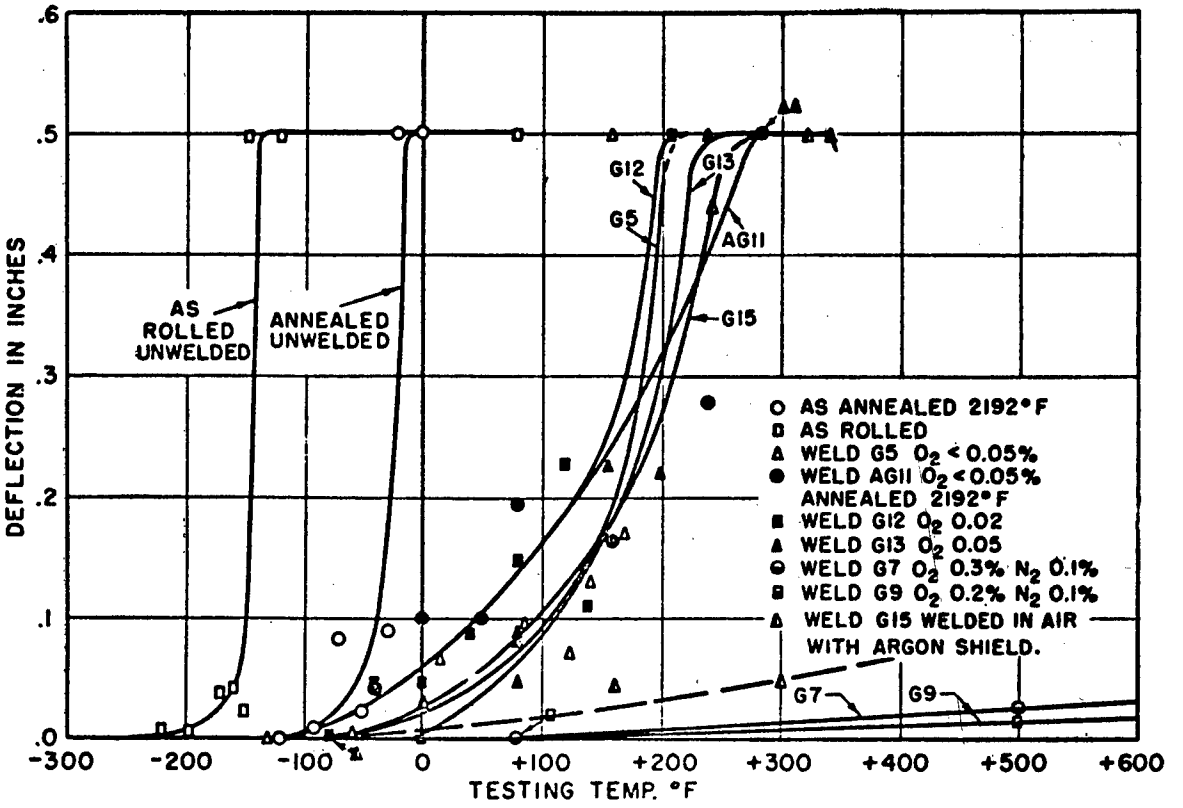


Fig. 35 - Deflection vs. Test Temperature for Molybdenum Welds Made in Argon With Oxygen Added.

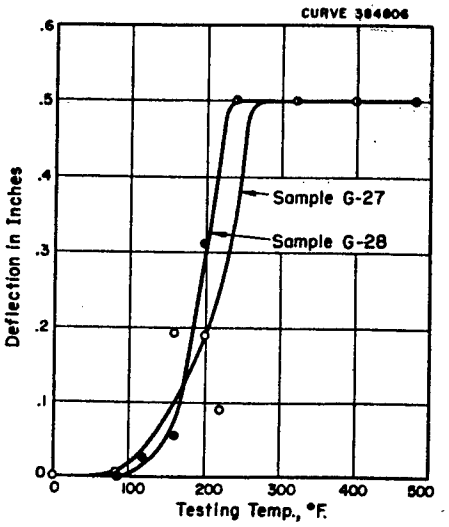


Fig. 36 - Relation Between Bend Deflection and Test Temperature for Welds Made in Atmospheres Containing 0.1% O_2, Balance Argon.

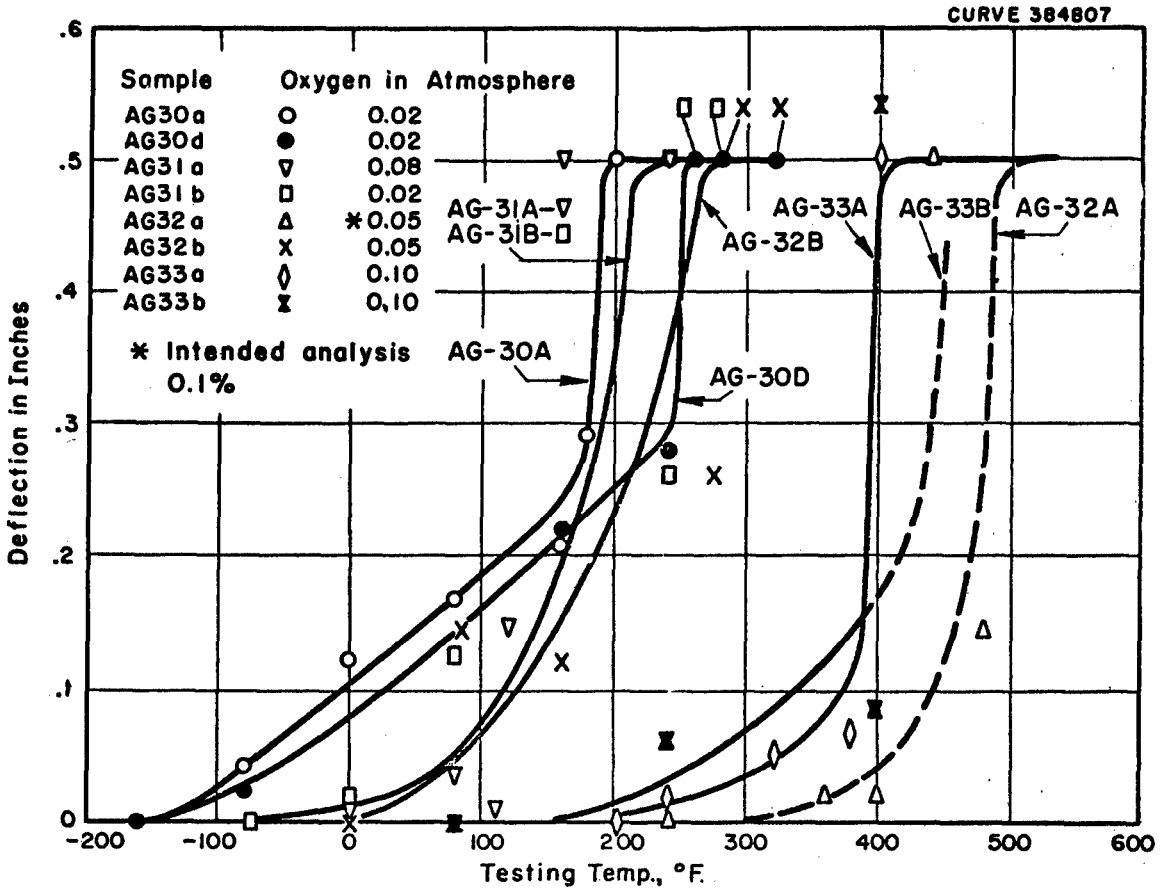


Fig. 37 - Relations Between Obtained Deflection and Test Temperature for Welds Made in Atmospheres Containing Oxygen.

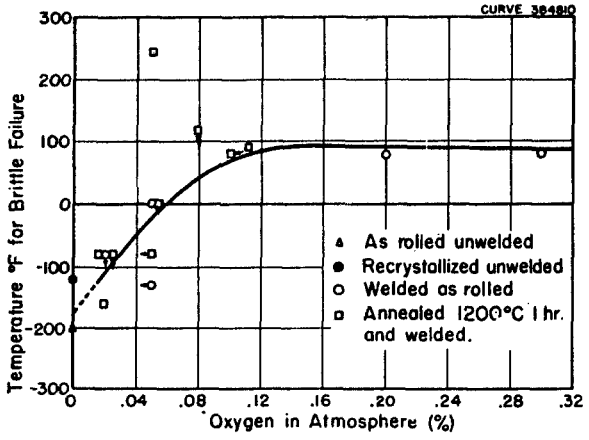


Fig. 38 - Temperature for Brittle Failure Related to Oxygen in Welding Atmosphere.

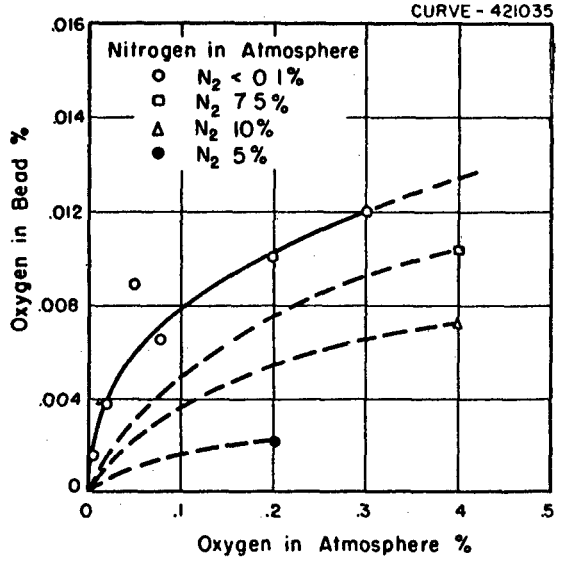


Fig. 39 - Oxygen Acquired During Welding As a Function of Oxygen and Nitrogen in the Welding Atmosphere.

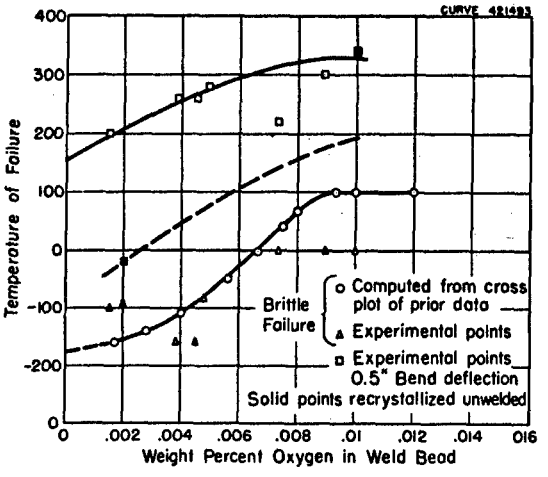


Fig. 40 - Relationship Between Oxygen in the Weld Bead, Brittle Failure Temperature and the Temperature for 0.5 In. Bend Deflections.

TABLE XIX

Oxygen content of weld beads and temperature of brittle failure and temperature of 0.4 in. deflection in arc-cast carbon deoxidized molybdenum as related to the welding atmosphere.

Sample	Atmosphere Analysis N_2	Atmosphere Analysis O_2	Bead Analysis % O_2 By Wt.	Temperature Brittle Failure	Temp. 0.4 in. Def. 100° Bend
G14	0.03	Nil	0.0015	-100°F	200°F
G15	Hand Torch With Argon Shield		0.0048	- 80	280
G27	0.1	0.1	0.0073	0	220
G30d	0.1	0.02	0.0038	-160	260
G32b	0.1	0.05	0.0089	0	300
SR1	0.1	0.05	0.0045	-160	260
As Recrystallized			0.002	- 90	- 20
N-O-12	0.1	0.3	0.010	0	340
N-O-14	0.1	0.3	0.012	-	-

weld metal during welding. The location of the points for the unwelded recrystallized material, Fig. 40, suggests that the increase in the weld grain size increases the temperature required to obtain a bend deflection of 0.5 in.

The decrease in the temperature required for brittle failure, Fig. 40, with decreasing oxygen in the weld metal may be explained by grain boundary films. The existence of such films has been established by Johnston and Wulff of Massachusetts Institute of Technology and Battelle investigators. The effectiveness of these films in changing the temperature of brittle failure can be closely related to the size of the grains in the weld bead. The curve for brittle fracture in Fig. 40 shows that there is a decrease in the temperature of brittleness with decreasing oxygen in the weld metal. At oxygen contents of 0.0085%, the temperature of brittle fracture is 100°F while welds with oxygen contents of 0.0015% do not become completely brittle above -160°F. An explanation of the change in the temperature of brittleness is found by considering the combined effect of grain size and oxide film thickness. If cylindrical grains are assumed in the weld area and the axes of these grains are assumed to have an angle of 45° with the plane of the sheet and with the axis of the weld bead the maximum length will be $t\sqrt{3}$, where t is the sheet thickness. The diameter, d, of a grain which will be covered with an oxide film β unit cells thick is given by Equation 1.

$$d = \frac{4\delta\beta C \; t\sqrt{3}}{\Delta \; t\sqrt{3} \; (4 W_o) - 2\delta\beta C} \qquad (1)$$

where
- d is the diameter of a grain in cm,
- δ is the density of the oxide, gm/cm^3, 6.47 for MoO_2,
- β is the number of unit cells of oxide,
- C is the dimension of unit cell which is monoclinic for MoO_2 and equals 5.526A,
- t is sheet thickness in cm, .152 cm for sheet used,
- Δ is the density of metal, gm/cm^3, 10.2 for Mo
- W_o is wt. % O_2 in molybdenum.

The development of this equation is given in Appendix I. This equation can be simplified by dropping the $2\delta\beta C$ term from the denominator. The value of this term is small and can be neglected as shown in Appendix I. Equation 1 may be further simplified by substitution of the constants as in Equations 2 and 3.

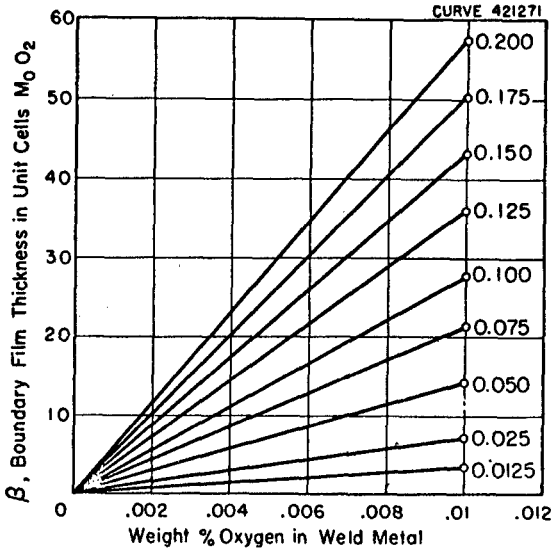


Fig. 41 - Relationship Between Oxygen in the Weld and Boundary Film Thickness.

$$d = \frac{37.6\beta}{10.7 \times 10^8 W_o} \qquad (2)$$

$$\beta = \frac{10.7 \times 10^8 W_o d}{37.6} \qquad (3)$$

For a given value of d, β is a linear function of W_o. A series of diameters from 0.0125 cm to 0.200 cm, 0.0049 in. to 0.079 in., was used and the relationship between W_o and β is shown, Fig. 41. These curves demonstrate the grain size effect as related to oxide films. The diameter of grains found on the weld bead surface was taken as d and falls in the range 0.01 to 0.03 in. or 0.0254 to 0.0762 cm[5]. Using the curve for brittle failure in Fig. 40, two oxygen contents were arbitrarily selected at 0.002 to 0.004%. The 0.002 value is near the oxygen content of the original molybdenum sheet, and the 0.004% value is one that is obtainable with commercial welding grade argon. In Fig. 41, the 0.002% oxygen content intersects the 0.025 and 0.075 cm diameter curve at β equals 1.5 and 4.5, and the 0.004% oxygen line intersects these curves at β equals 3.0 and 8.5. Thus at oxygen contents of 0.004% and with a grain diameter of 0.075 cm, the grain boundary film would be 47×10^{-8} cm thick, assuming that all the oxide is in the grain boundary and that the film is continuous. A film of this thickness would not be resolved at 2000X where the resolving power is 5×10^{-6}. However, the effectiveness of these films diminishes below 0.002% oxygen. It is believed that if the limit of the oxygen in the weld metal can be held below 0.002% the temperature for brittle failure will approach that of the unwelded plate in the recrystallized material.

It is possible to predict the requirements of the welding atmosphere with respect to oxygen from the grain size of the material in the weld and the molybdenum oxide film thickness which will cause the material to behave in a brittle manner. If the value of 0.002% oxygen is used with a grain size of 0.025 the condition for brittle behavior shifts with grain size as

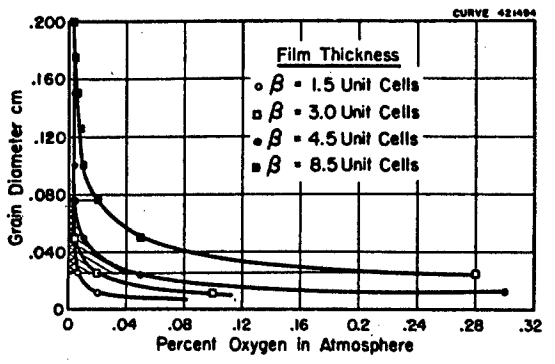


Fig. 42 - Oxygen in Weld Bead and Grain Size for Several MoO_2 Film Thicknesses.

shown in Fig. 42. This relationship shows that the oxygen in the welding atmosphere must be below 0.003% to avoid brittle behavior in the larger grains. However, if the larger grains are the controlling factor in the fracture behavior as they would seem to be, since the oxygen tolerance is smaller with increased grain size for a given film thickness, then the curve derived from the value of β equals 4.5 should be used. The oxygen tolerance for grains 0.075 cm in diameter is then 0.004% and the upper limit is 0.04% for grains 0.025 cm in diameter. It is most important to note that if in some manner the grain size of the weld zone could be decreased the tolerance for oxygen could be increased. It is possible that additions of a material which is nonvolatile and does not wet the grain boundaries in any form would restrict the grain growth in the weld bead. From earlier work in deoxidization of vacuum sintered molybdenum, Ti_2O_3 would seem to meet the requirements and should be tried.

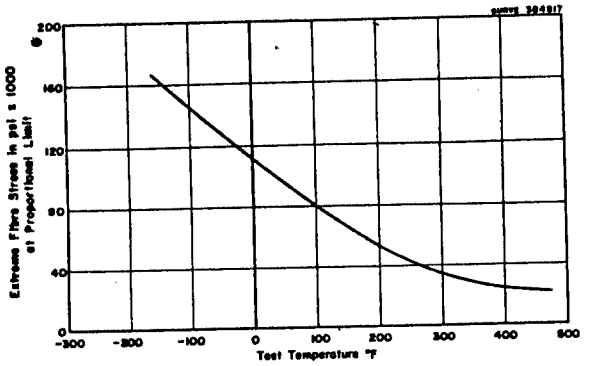
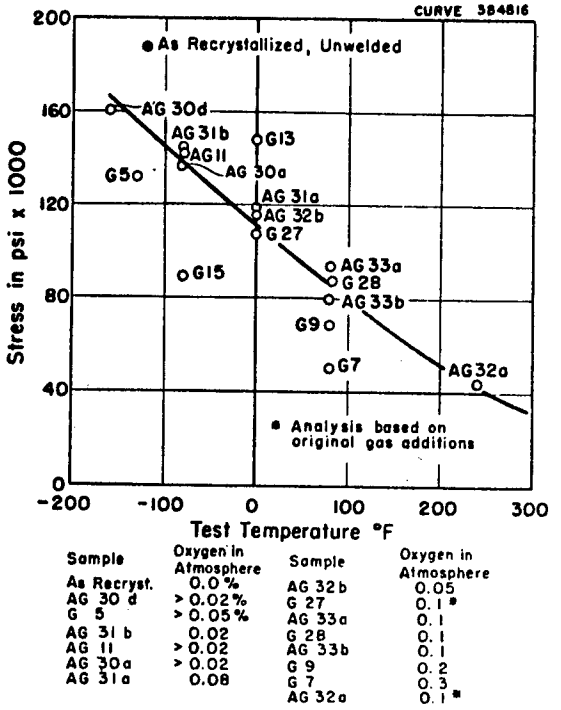


Fig. 43 - Curve showing relation of calculated fiber stress at proportional limit as related to test temperature for welds made in oxygen bearing atmospheres.

Most body centered cubic metals show an increase in the stress at the proportional limit with decreasing temperature. Molybdenum follows this general pattern. A curve was obtained for arc-cast carbon deoxidized molybdenum weld metal. This curve, Fig. 43, is a composite of a large number of curves from a number of different samples and the actual points are not plotted. The data used to plot Fig. 43 were computed from the bending equation and apply to the outer fiber of the bend test specimens. This curve has been replotted in Fig. 44, and the points



Sample	Oxygen in Atmosphere	Sample	Oxygen in Atmosphere
As Recryst.	0.0 %	AG 32 b	0.05
AG 30 d	> 0.02 %	G 27	0.1 *
G 5	> 0.05 %	AG 33a	0.1
AG 31 b	0.02	G 28	0.1
AG 11	> 0.02	AG 33b	0.1
AG 30a	> 0.02	G 9	0.2
AG 31a	0.08	G 7	0.3
		AG 32a	0.1 *

Fig. 44 - Relation Between Fiber Stress at Brittle Failure and Test Temperature for Welds in Oxygen Bearing Atmospheres.

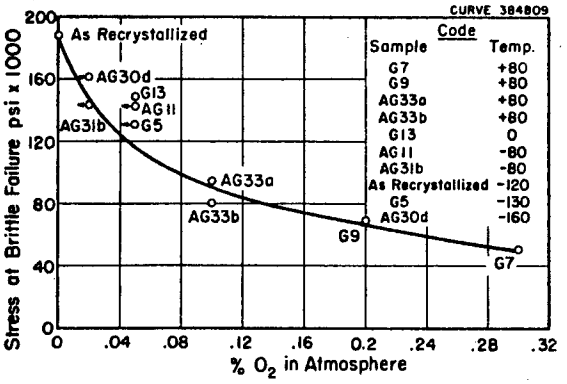


Fig. 45 - Relation Between Stress at Brittle Failure and Oxygen Content of Welding Atmosphere.

for brittle rupture are shown for a number of samples welded in atmospheres containing various amounts of oxygen. As the oxygen in the welding atmosphere is increased the stress at brittle rupture decreased along the stress at the proportional limit curve. There are a few exceptions to this relationship but these exceptions may be explained by the drop in the stress required for rupture with decreasing temperature after the temperature for brittle rupture has been reached. However, it is apparent from these data that, as the oxygen in the welding atmosphere increased, the temperature for completely brittle failure increases according to the function given for the relation of stress at the proportional limit to the test temperature. The relationship between the oxygen in the welding atmosphere and the brittle rupture stress is shown in Fig. 45. When the oxygen in the weld bead is related to the stress for brittle failure the stress decreases with the oxygen content according to the relationship shown in Fig. 46. The upper point on this curve is for unwelded recrystallized material and this point follows the data for the weld metal

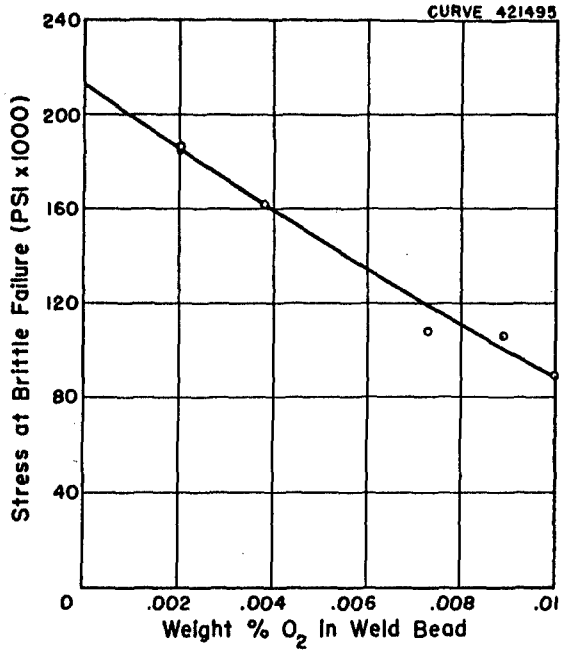


Fig. 46 - Relationship Between Oxygen in the weld and Stress at Brittle Failure.

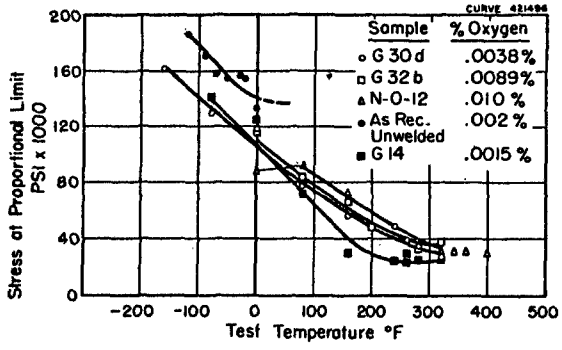


Fig. 47 - Effect of Oxygen in the Weld Metal on the Stress at Proportional Limit Vs. Temperature Curves.

Examination of the stress at the proportional limit data for welds with known oxygen contents brought out the fact that the oxygen in the weld causes a premature rise in the stress at proportional limit-temperature relationship. An examination of Fig. 47 shows that the proportional limit starts to rise at a lower temperature when the oxygen in the weld metal is at a minimum. Thus far the lowest oxygen content found in a weld bead was 0.0015%, Fig. 47. However, the slope of the stress at proportional limit-temperature curve is apparently a function of some other variable.

The data shown on the effect of oxygen on the stress at the proportional limit and the stress at brittle rupture indicate that as the oxygen in the weld metal is increased the stress required for brittle rupture decreases and the temperature at which such failure occurs increases depending on the stress at proportional limit relationship. The temperature at which the stress at the proportional limit begins to rise depends on the oxygen content of the weld metal and the effectiveness of the oxygen depends on the grain size of the material. The effect of grain size is indicated by the dotted portion of the curve for recrystallized material, Fig. 47. This dotted section is justified by the fact that the point at 0°F attained a maximum deflection in bending and other data indicate that while this condition exists the stress at the proportional limit remains reasonably

constant. The grain size of the recrystallized material was much smaller than the as-welded samples. Thus the temperature of brittle behavior is related to the oxygen content of the weld metal and the grain size through the stress at the proportional limit relationship.

The fractured surfaces of the bend test specimens made in atmospheres bearing oxygen in the range 0.02% to 0.3% were studied to determine the nature and origin of fracture. The examination showed that the origin of fracture was predominately intergranular. From a total of 62 specimens examined, 57 had their fracture origin in the grain boundaries, one was in the grain and four were of doubtful origin. However, after the fracture has started the path of the fracture may be either transcrystalline or intercrystalline. Only the samples welded in relatively high oxygen containing atmospheres were completely intergranular. In general, the specimens examined were more than 50% transgranular in spite of the intergranular origin of fracture. In a few cases the only intergranular surface in the fracture was found to be the origin of fracture. After the fracture has started the amount of transgranular fracture surfaces in the specimens increases with the temperature of testing. In general, the fracture study confirmed the other data which indicated that the fracture strength was a function of the grain boundary strength. It appears that the grain boundaries are the weakest point in the material and as the temperature of testing is decreased and the stress at the proportional limit is increased the grain boundary having the most nearly complete or the thickest film of oxide will be the first to fail. This confirms observations made earlier in this report.

It has definitely been established that oxygen in the weld metal will reduce the ductility of the material. The mechanism involved is dependent on grain boundary film formation. Thus it appears that in order to reduce the effects of oxygen on weld ductility to a minimum, it is necessary to eliminate or minimize these boundary films. Two factors control the effectiveness of oxygen in the weld metal, the oxygen concentration in the weld metal and the size of the grains in the weld metal. The oxygen in the weld metal may be reduced to a minimum by careful atmosphere control as indicated in Fig. 42. However, the control of the grain size in the weld metal will require the addition of some material which will restrict the grain size. It is believed that a material such as titanium which forms

nonvolatile oxides at welding temperatures and does not wet the grain boundaries could be used. The oxide of titanium has been found to form spherical particles which could restrict the growth of the grains during solidification. The use of molybdenum which has been deoxidized with titanium is strongly suggested.

Welds in Nitrogen Bearing Atmospheres

Since the sources of cracking, porosity and low ductility in molybdenum welds were not originally known, it was decided to investigate the obvious sources of contamination first. In any shielded welding process, regardless of the method of shielding, contamination from the presence of the air components, nitrogen and oxygen, is always possible. The effects of oxygen have already been discussed. It was believed that nitrogen could be easily acquired by the molten molybdenum weld puddle because a portion of the nitrogen in the arc would be in the atomic and ionized forms.[14] Nitrogen atoms are sufficiently small to exist as an interstitial element and can enter the molybdenum lattice when in the atomic state. This combination of factors strongly suggested that the effects of nitrogen be studied with respect to the weld quality and physical properties.

Weld test beads were made in carbon deoxidized molybdenum using incremental additions of nitrogen to an argon atmosphere. The nitrogen in the atmosphere was varied from 0.1% to 85% with the remainder in each case consisting of argon. No deliberate additions of oxygen were made in these tests. Welding data are given in Table XX. The welding current was maintained at 180 amps. The arc voltage shifted with the nitrogen concentration in the welding atmosphere as shown in Fig. 48. The amount of material melted with a given arc travel speed and welding current increased with the nitrogen concentrations and reflects the increase in the arc energy due to nitrogen additions. Melting may also have been increased by the reduction in the melting point due to a molybdenum nitrogen eutectic. The presence of such a eutectic seems doubtful because hot center bead cracking was not observed in weld beads made with nitrogen additions up to 50%. Both hot tears and gross porosity occurred with 85% nitrogen in the welding atmosphere. Crater cracks occurred in all welds made with 2.5% nitrogen and over in the arc atmosphere.

TABLE XX

WELDING DATA FOR WELDS MADE WITH NITROGEN ADDITIONS TO THE ATMOSPHERE

Sample	Atmosphere Analysis	Weld Current Amperes	Weld Voltage	Arc Travel Speed In./Min	Comments
G18	A 92% N_2 8%	170	13-14	7.35	Clean, bright bead. Flow lines in bead formed while cooling.
G18a	A 92% N_2 8%	175	14	6.36	Bright, clean bead. Strain lines. Some arc blow.
G19	A 75% N_2 25%	180	13.5	6.02	Difficulty with high frequency stabilizer. No spark. Increased gap to .038. Arc length may have been in error. Weld clean, bright.
G20	A 70% N_2 30%	180	15.5	5.6	No crack after welding. Cracked through crater three days later upon slight flexing.
G21	A 50% N_2 50%	170	17	5.9	Clean, bright bead. Crater cracks.
G22	A 98.5% N_2 1.5%	185	13	6.2	Clean, bright bead but narrow. 90-100% penetration. Crater crack.
G23	A 97.5% N_2 2.5%	175	12.5	6.75	Clean, bright bead. No visible cracks.
G24	A 99.0% N_2 1.0%	180	12.5	6.75	Clean, bright, narrow bead, no cracks.
G25	A 99.9% N_2 0.1%	180	12.5	6.15	Clean, bright, narrow bead, no cracks.
G26	A 15% N_2 85%	170	19	6.45	Wide rough bead, porosity in crater. Hot tears near end of bead. Arc had difficulty starting.

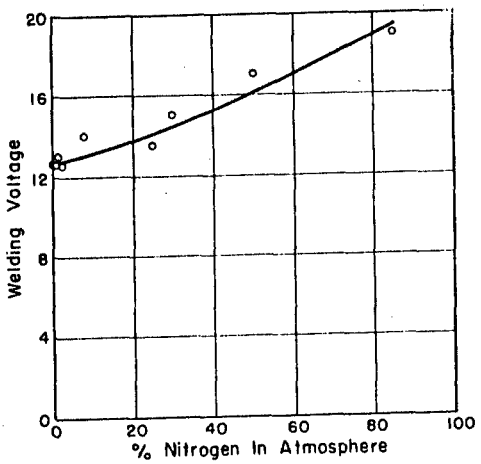


Fig. 48 - Welding Voltage vs. Nitrogen in Atmosphere

Fig. 49 - Arc-Cast Molybdenum Welded in Argon With 0.1% N_2 Added. Sample G25.

Fig. 50 - Arc-Cast Molybdenum Welded in Argon With 50% N_2 Added. Sample G21.

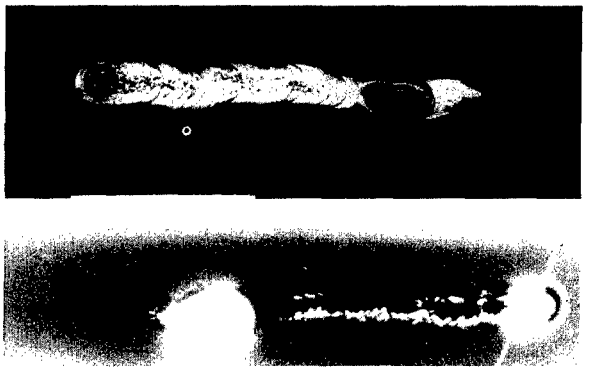


Fig. 51 - Arc-Cast Molybdenum Welded in 15% Argon, 85% N_2. Sample G26.

Weld beads made in low and high nitrogen atmospheres are shown with their X-ray pictures in Figs. 49 to 51. The increase in bead width can easily be seen with respect to the increase in nitrogen concentration in the atmosphere. The absence of hot center bead cracks is evident. Porosity is observed only in the specimen made under an atmosphere of 85% nitrogen.

The molten molybdenum acquires nitrogen during the welding operation. Analyses data for the welds made in nitrogen bearing atmospheres are shown in Table XXI and this relationship is shown in Fig. 52. This curve shows that the major portion of the nitrogen is acquired by the weld metal when the nitrogen is less than 1% in the welding atmosphere. Welding grade argon frequently contains 0.1% nitrogen. The nitrogen acquired by the weld metal in the chamber

tests at this concentration was 0.055% as compared to 0.003% in the original sheet stock. The amount of nitrogen in welds made with welding grade argon would be expected to contain a minimum of 0.055% nitrogen.

TABLE XXI

NITROGEN PICKED UP BY MOLYBDENUM DURING WELDING IN ARGON-NITROGEN ATMOSPHERES

Sample No.	Percent Nitrogen In Atmosphere	Percent Nitrogen In Weld Bead
G25	0.1	0.055
G24	1.0	0.068
G22	1.5	0.067
G23	2.5	0.163
G18	8.0	0.081
G19	25.0	0.086
G20	30.0	0.088
G21	50.0	0.115
G26	85.0	0.090
AG30	0.1	0.02
Unwelded	-	0.003

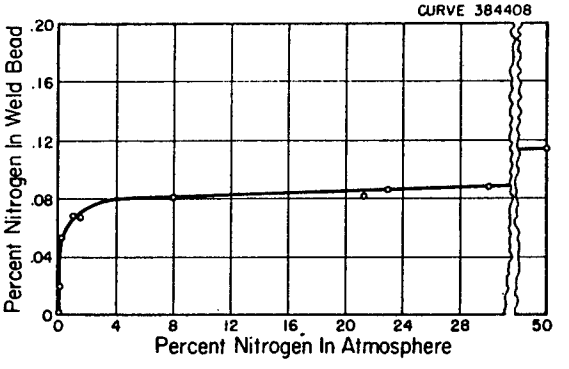
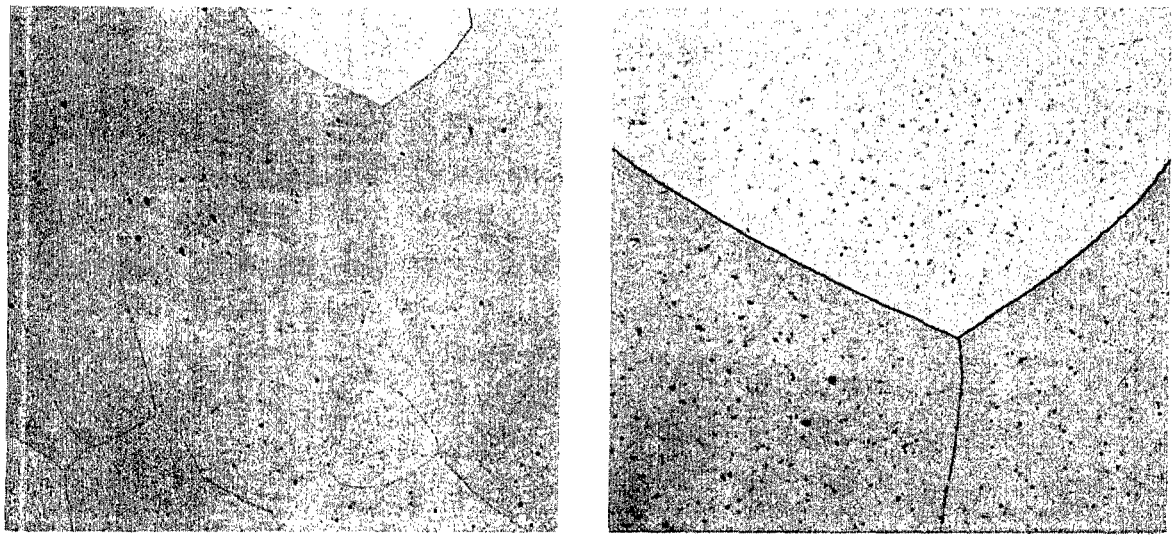


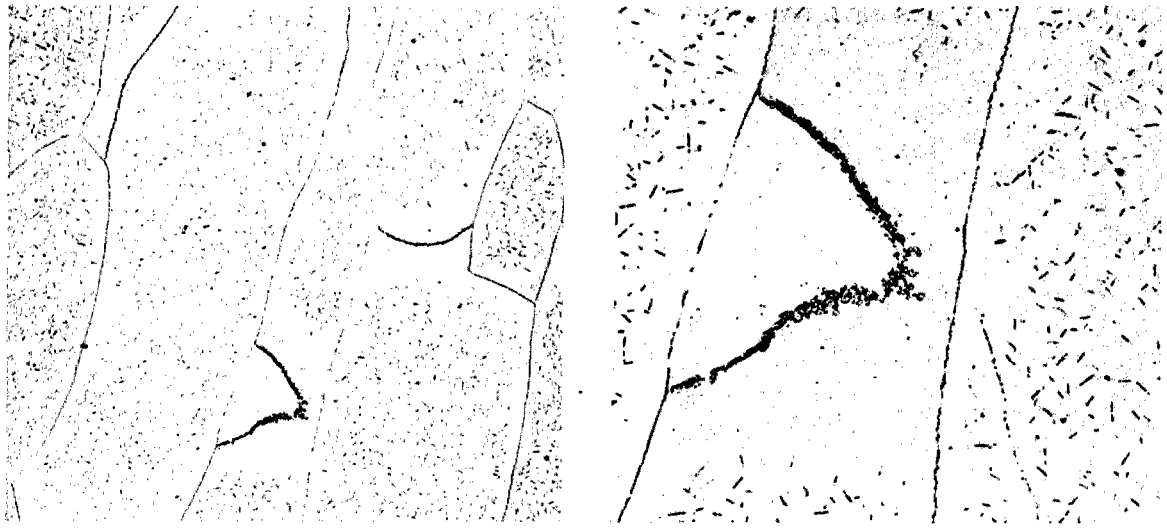
Fig. 52 - Nitrogen in Weld Bead vs. Nitrogen in Atmosphere.

Metallographic examination of the weld metal fused under nitrogen bearing atmospheres shows that the nitrogen is present as nitrides. As the nitrogen in the atmosphere is increased the number and size of the nitrides formed in the weld metal increases. The photomicrographs shown in Figs. 53 to 56 indicate that as the nitrogen content of the weld increases, the tendency to form grain boundary films and nitrides in the grain matrix both increase. Near the grain boundary the nitrides in the grain matrix have been greatly



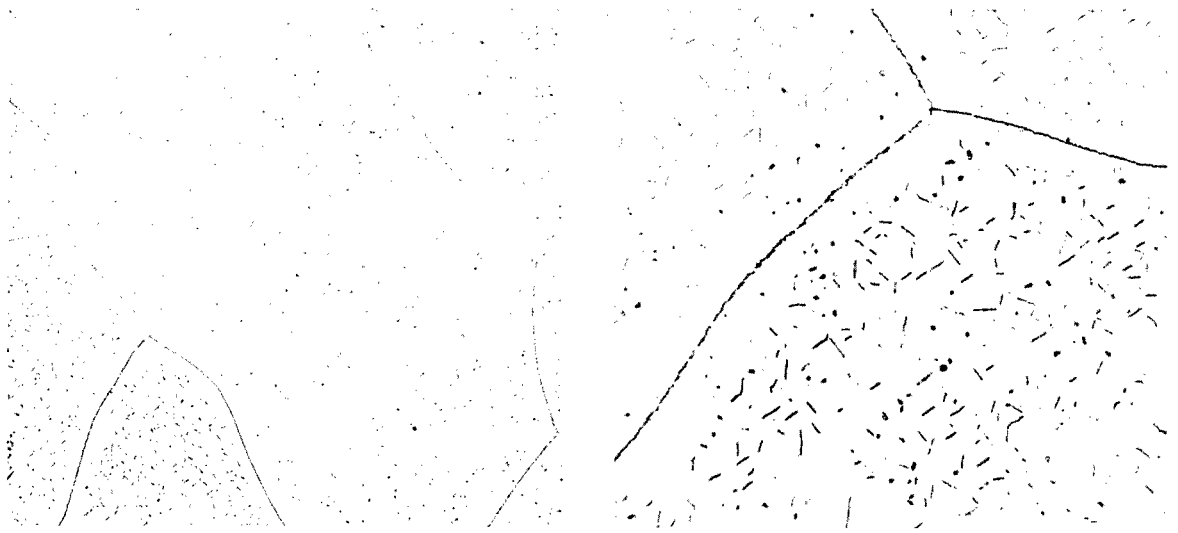
(a) P53-225-2 100X (b) P53-225-8 300X

Fig. 53 - Weld Zone in Weld G25. Weld Bead 0.055% N.



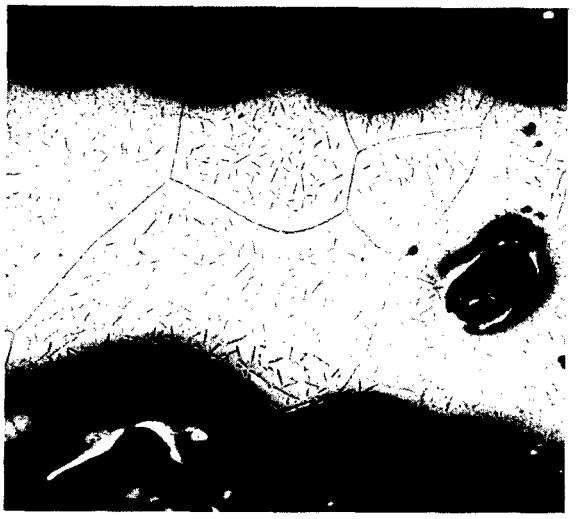
(a) P53-210-2 100X (b) P53-210-8 300X

Fig. 54 - Weld Zone in Weld G18a. Welding Atmosphere 8% N_2, Weld Bead 0.081% N.



(a) P53-210-5 100X (b) P53-210-11 300X

Fig. 55 - Weld Zone Sample G21. Welding Atmosphere 50% N_2, Weld Bead 0.115% N.



P53-210-6 100X

Fig. 56 - Weld Zone Sample G26. Welding Atmosphere 85% N_2, Weld Bead 0.090% N.

reduced and these nitrides appear to be precipitated at the grain boundaries. Heavy, continuous films appeared in the boundaries when the nitrogen concentration exceeded 0.067%. The relationship between these boundary films and the mechanical properties will be discussed later.

The welds made in atmospheres containing nitrogen in the range 0.1% to 85%, with the balance argon, were tested in bending over a range of temperatures. The bend test data are given in Table XXII. The relationship between the bend deflection and the temperature of testing is shown in Fig. 57. Increasing

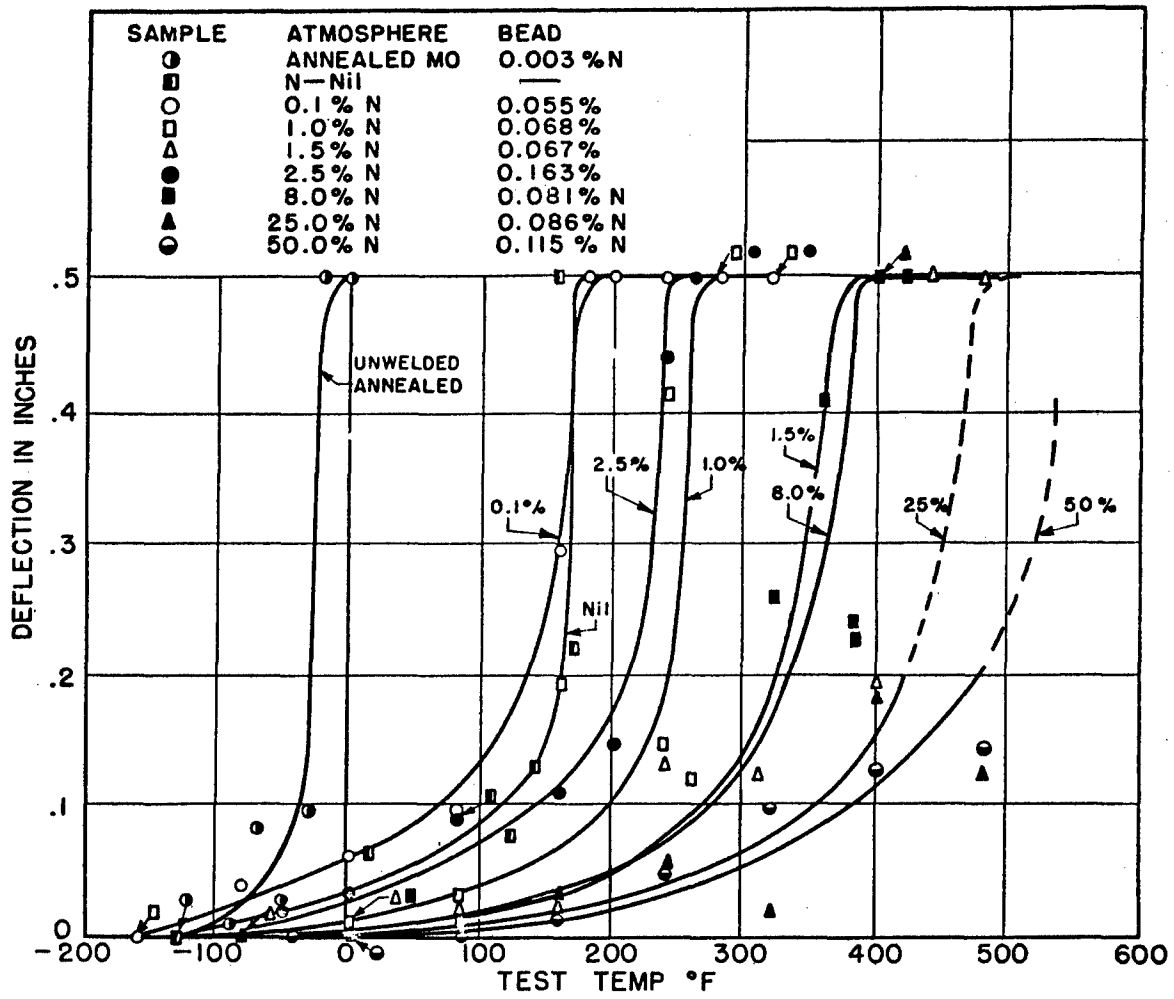


Fig. 57 - Deflection vs. Test Temperature for Weld Made in Argon With Various Amounts of Nitrogen Added.

the nitrogen in the welding atmosphere shifts the temperature of maximum ductility to higher temperatures. This relationship is clarified if the percent nitrogen in the weld bead is related to the temperature at which

TABLE XXII

BEND TEST DATA FOR SAMPLES WELDED IN NITROGEN-BEARING ATMOSPHERES

Spec. No.	Nitrogen Addition to Arc Atmosphere	Test Temp. °F	Thickness	Width	Load at Prop. Limit Lbs.	Max. Load Lbs.	Load At Fracture Lbs.	Inches Deflection at Fracture
G25	0.1%	320	.060	.2515	19	55	-	No Fracture
	0.1	280	.059	.2515	13	56	-	No Fracture
	0.1	240	.0595	.2515	23	57.8	-	No Fracture
	0.1	200	.0595	.2515	19	63	-	No Fracture
	0.1	180	.059	.251	34.5	62	-	No Fracture
	0.1	160	.060	.2495	39.5	65	59.5	.295
	0.1	79	.060	.251	54	-	79.4	.097
	0.1	0	.0595	.251	72	-	100	.063
	0.1	- 80	.060	.2515	76	-	104	.039
	0.1	-160	.0595	.251	-	-	106	-
G24	1.0	320	.0595	.248	18	57	-	No Fracture
	1.0	280	.0505	.250	10	38	-	No Fracture
	1.0	260	.060	.248	17.5	-	54	.119
	1.0	240	.057	.248	28.2	52.8	39	.412
	1.0	240	.060	.248	20	-	59.5	.149
	1.0	160	.060	.250	38	-	67	.193
	1.0	79	.058	.2485	48	-	64	.029
	1.0	0	.060	.250	66	-	83	.009
	1.0	- 80	.0525	.249	63	-	75	.002
	1.0	-160	.060	.2505	90	-	101	.002
G22	1.5	480	.059	.252	12	54	-	No Fracture
	1.5	440	.060	.252	13	54	-	No Fracture
	1.5	400	.0595	.252	12	-	53	.192
	1.5	320	.060	.2525	16.3	-	53	.126
	1.5	240	.059	.2525	28	-	58.2	.132
	1.5	160	.0595	.2525	38.8	-	52	.023
	1.5	79	.0595	.2525	50	-	66	.017
	1.5	0	.0595	.2525	64	-	81.5	.009
	1.5	- 80	.059	.2515	77	-	90	.002
G23	2.5	320	.060	.2505	13	51	-	No Fracture
	2.5	280	.060	.2505	16.5	51.2	-	No Fracture
	2.5	260	.0595	.2505	15	55.7	-	No Fracture
	2.5	240	.0595	.251	17	54	40	.438
	2.5	200	.060	.251	18	-	60	.147
	2.5	160	.055	.2505	18	-	49.5	.110
	2.5	82.5	.055	.2505	39	-	63	.087
	2.5	0	.0595	.2505	63	-	82	.036
	2.5	- 80	.053	.2505	63	-	76	.003
G18A	8.0	420	.060	.2505	14	52.5	-	No Fracture
	8.0	400	.060	.251	15.5	54	-	No Fracture
	8.0	380	.060	.2515	16	56.2	55.8	.238
	8.0	380	.060	.251	15.5	-	56.5	.225
	8.0	360	.060	.251	13	56	43.5	.407
	8.0	320	.0595	.251	17	58	57	.257
	8.0	82.5	.0595	.251	50	-	64	.012
	8.0	0	.0595	.250	73	-	84	.009
G19	25.0	480	.0595	.250	12	-	46	.123
	25.0	400	.059	.250	13	-	56	.183
	25.0	400	.0595	.250	15.5	61.5	-	No Fracture
	25.0	320	.059	.250	16.5	-	36.5	.017
	25.0	240	.059	.250	21	-	48	.058
	25.0	160	.0595	.250	39	-	51.5	.029
	25.0	82.5	.059	.250	51	-	62	.004
	25.0	0	.059	.250	66	-	78	.002
	25.0	- 80	.0595	.2495	-	-	73	-
G20	30.0	420	.057	.246	17	50	-	No Fracture
	30.0	400	.0585	.250	13	54.2	-	No Fracture
	30.0	380	.059	.250	14	54.5	52.5	.283
	30.0	360	.049	.250	12	-	35.8	.188
	30.0	320	.0575	.245	16.2	-	46.3	.120
	30.0	240	.0575	.250	28	-	47.3	.076
	30.0	160	.054	.2485	34	-	46	.057
	30.0	79	.052	.250	38.8	-	50	.029
	30.0	0	.054	.2455	57	-	67.5	.009
	30.0	- 80	.054	.249	66	-	75.5	.002
G21	50.0	480	.059	.250	13	-	56	.142
	50.0	400	.059	.2505	8	-	50.5	.126
	50.0	320	.059	.251	7.5	-	54.5	.097
	50.0	240	.059	.251	14	-	48	.054
	50.0	160	.056	.251	37.3	-	45	.014
	50.0	79	.059	.251	58	-	66.5	.003
	50.0	0	.0565	.250	66	-	76.5	.004
	50.0	- 40	.059	.251	-	-	72	-
	50.0	- 80	.059	.2505	-	-	86.5	-

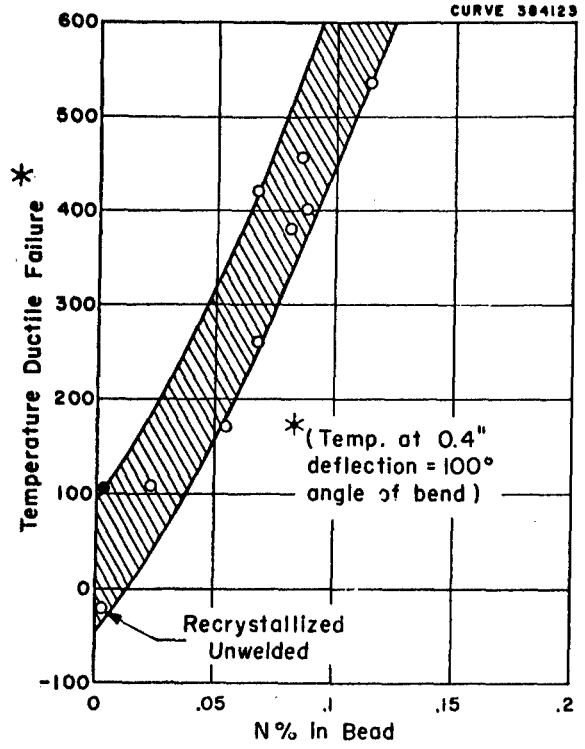


Fig. 58 - Relation Between Ductile Failure Temperature*(^{o}F) of Bend Specimen and Nitrogen in Weld Bends.

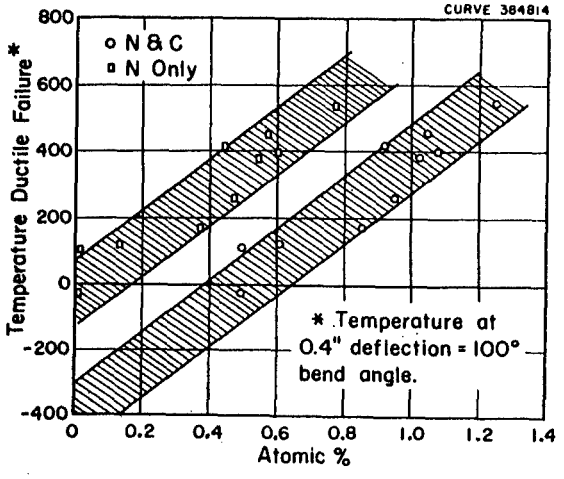


Fig. 59 - Relation Between Transition Temperature* (^{o}F) and Atomic Percent Carbon and Nitrogen in Weld Bead.

ductile behavior is obtained in bending, Fig. 58. This transition temperature was taken arbitrarily as the temperature at which 0.4 in. deflection or 100° angle of bend was obtained. From this curve it appears that as the nitrogen content of the weld metal is decreased the temperature at which 0.4 in. deflection will be obtained is decreased. One of the points shown for the minimum nitrogen concentration was obtained from a weld made in helium which is low in nitrogen. The other point is not strictly applicable because it applies to unwelded recrystallized material and the effect of grain size becomes a factor. However, this point falls in the scatter band of the data obtained for welded material. Other variables may influence the relationship shown in Fig. 58. For example, these data do not consider the effect of carbon in the weld metal. Carbon is also an interstitial element and has a behavior similar to nitrogen. Nor do these data allow for the effects of oxygen which is known to be present in the welding atmosphere in amounts of 0.02% to 0.05%. This amount of oxygen could influence the fracture characteristics of molybdenum weld metal as was shown earlier.

The possible effects of carbon and nitrogen upon the ductility of weld beads can best be shown by considering the atomic percent of these elements in the weld bead,

Fig. 59. Chemical analysis of the weld metal has shown that the carbon content of the weld is not reduced during the welding operation. The carbon content of the material before and after welding was 0.06% by weight. Data have been calculated for the atomic percent of the nitrogen and carbon found in the weld bead, Table XXIII.

TABLE XXIII

BRITTLE FRACTURE STRESS AND NITROGEN CONCENTRATION DATA

Sample	Brittle Failure Temp. °F	Ductile Failure Temp. °F	Outer Fibre Tensile Stress For Brittle Failure	Atomic % N + C	Nitrogen In Bead Weight %	Nitrogen In Bead Atomic %	Nitrogen in Atmos. %
G21	- 80	540	149,000	1.25	0.115	0.77	50.0
G21	- 40	-	124,000	1.25	0.115	0.77	50.0
G20	- 80	400	135,000	1.08	0.090	0.60	30.0
G19	- 80	460	124,500	1.05	0.085	0.57	25.0
G18a	0	380	124,500	1.02	0.080	0.54	8.0
G23	- 80	230	132,000	1.57	0.163	1.09	2.5
G22	- 80	420	133,000	0.93	0.067	0.45	1.5
G24	- 80	260	137,500	0.93	0.068	0.45	1.0
G24	-160	-	150,000	0.93	0.068	0.45	1.0
G25	-160	170	182,000	0.85	0.055	0.37	0.1
G30A	-160	120	101,000	0.61	0.020	0.13	0.1
As Rolled	-120	- 30	185,000	0.49	0.002	0.01	0.0
He 1	-240	120	201,000	0.50	0.003	0.02	0.0

The temperatures of completely ductile behavior, plotted against the atomic percent of N and N + C, Fig. 59, show that where data is available, the transition temperature decreases directly with the decreases in the total atomic percent of N and N + C. An extrapolation of these data suggests that if the total nitrogen and carbon in the weld metal were maintained at a sufficiently low value it would be possible to obtain ductile weld metal at temperatures below ambient. The relationship may not remain linear below 0°F so that the minimum temperature for ductile behavior could be higher than indicated in Fig. 59. It should be remembered that these data are not independent of the effects of oxygen. Oxygen in the welding atmosphere could cause boundary

films which shift the ductility characteristics or it could by an oxidizing action remove a portion of the carbon from the weld metal. A further effect of oxygen on weld properties which will be discussed at length in another section is the ability of oxygen to counteract the effect of nitrogen and vice versa when in the welding arc. Apparently the oxygen and nitrogen react, and in the welding chamber used, the products of this reaction were removed from the weld area so that the amount of both oxygen and nitrogen may be lower than would be expected for a given concentration of either one. In the event of the removal of nitrogen or carbon in such a way as to reduce the total amount of interstitial elements in the weld metal, the curve in Fig. 59 would be shifted to the right.

The temperature for completely brittle fracture is raised by nitrogen additions to the welding atmosphere. Table XXIII shows the brittle fracture data for welds made in nitrogen bearing atmospheres. The correlation between nitrogen in the weld bead and the temperature of brittle fracture is shown in Fig. 60. A general trend is shown and as the nitrogen decreases the temperature of complete brittleness decreases. In Fig. 61, a similar plot is shown for the atomic percent of nitrogen plus carbon. The data in this curve suggest again that the temperature of complete brittleness may be reduced by reducing the concentration of interstitial elements to a minimum.

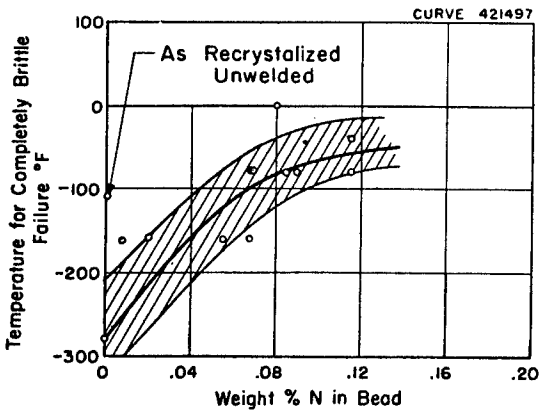


Fig. 60 - Effect of Nitrogen in Molybdenum Weld Beads on the Temperature for Brittle Fracture.

The relationship between the stress required for fracture and the nitrogen concentration is shown in Fig. 62. The relationship here is somewhat uncertain because of insufficient data, but there is a strong indication that the stress at the proportional limit is not shifted by nitrogen additions above 0.07%. A similar effect on the temperature for brittle failure can be observed in Figs. 60 and 61. The data suggest that the temperature of completely brittle behavior does not increase with increased

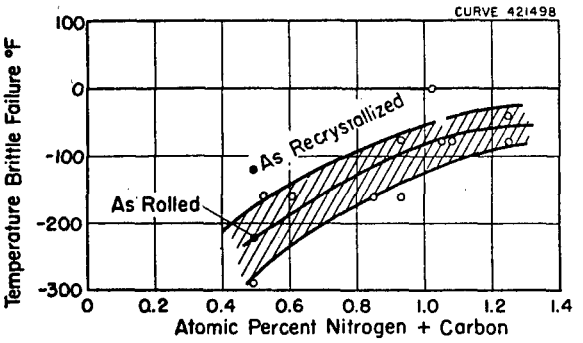


Fig. 61 - Effect of Nitrogen and Carbon in Molybdenum Weld Beads Upon the Temperature of Brittle Failure.

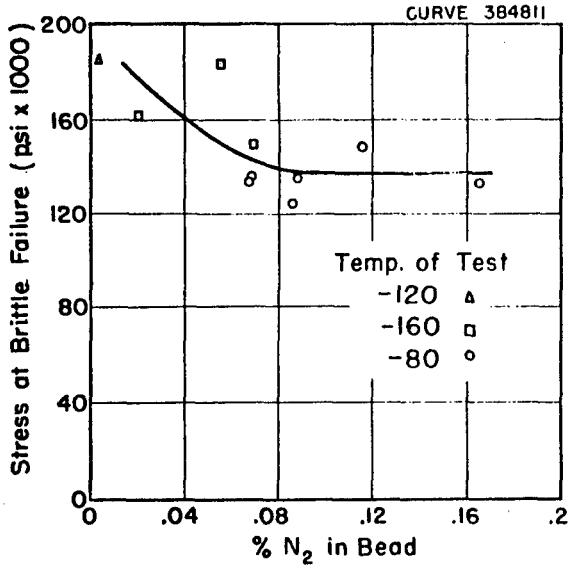


Fig. 62 - Effect of Nitrogen in Molybdenum Weld Beads Upon the Brittle Rupture Stress.

nitrogen in the weld metal when the nitrogen concentration exceeds 0.07%. However, nitrogen concentrations below 0.07% cause the stress for brittle fracture to increase and the temperature for failure to decrease as the nitrogen is progressively decreased.

An explanation for the change in properties can be seen in part by an examination of the metallographic samples of welds made in nitrogen bearing atmospheres, Figs. 53 to 56. These photomicrographs show that the nitrides tend to form first in the grain boundaries and later in the body of the grain. The combination of mechanical property data with the metallographic data suggests that with less than 0.07% nitrogen in the bead the boundary film of nitrides tends to become discontinuous. This condition could account for the reduction of the brittle fracture strength with nitrogen concentrations less than 0.07%.

The boundary films implied intergranular fractures. A study of the fracture origins on the bend test specimens from welds made in nitrogen bearing atmospheres showed that of 60 specimens 54 had intergranular fracture origins. From the remaining six specimens, two were definitely transgranular and four were of doubtful origin. This breakdown was nearly the same as found for the samples welded in oxygen bearing atmospheres. However, in the case of samples welded in oxygen the brittle failure stress continued to decrease with increased oxygen concentration along the stress at proportional limit vs. temperature curve shown in Fig. 43. Weld beads with nitrogen

above 0.07% did not show this effect. A possible explanation for the difference in the effects of these two gases may lie in the micro-mechanism of fracture.

Fracture may depend upon the effects of interstitial elements which tend to reduce the ability of the material to receive cold deformation. This is demonstrated by the effect of N and C on the temperature of maximum bend ductility. It appears that nitrogen and carbon may prevent the movement of dislocations by the formation of obstacles. Such obstacles could be in the form of interstitial atoms, N or C, in solution in the BCC lattice or in the form of nitrides or carbides. An increase in the number of obstacles would cause the material to reach a condition where the dislocations are no longer free to move and the grain does not plastically deform without excessive stress. It has been demonstrated by Zener[15] that if the grains of a material are unable to plastically deform, hydrostatic type stresses are applied to the point of intersection of three grains and when this stress reaches a sufficiently high value fracture will result in the grain boundary. The action of nitrogen and carbon in reducing the ability of the grains to receive plastic deformation plus the action of the oxide and nitride films in the grain boundaries should produce the types of intergranular fracture origins found in these investigations. It would also appear that the mobility of the dislocations is reduced to a critical level by the nitrogen in the weld metal in amounts over 0.07% at temperatures below -80°F. Under these conditions the material would fail in the grain boundaries depending on the amount of boundary film present. Oxide or nitride films could have been formed during welding with the atmospheres used, and these films would have been sufficiently thick to produce the reduction in fracture strength shown if the grain matrix was unable to receive plastic deformation.

The data obtained on the effects of nitrogen in molybdenum weld beads indicate that if welds of maximum ductility are to be obtained, the amount of interstitial elements, nitrogen and carbon, must be maintained at a minimum level. The oxygen level must also be maintained within the limits discussed earlier if full advantage is to be taken of the reduction in the interstitial elements in the weld metal.

Welds Made in Atmospheres Containing Oxygen and Nitrogen

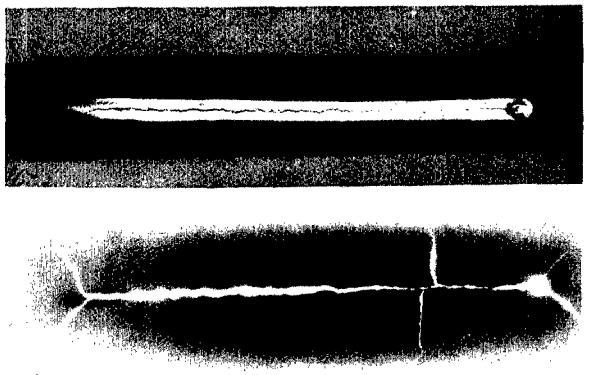
A series of welds were made in atmospheres covering a range of oxygen and nitrogen contents. Two fixed oxygen levels were used, 0.2% and 0.4%. Data presented earlier in this report have indicated that oxygen in the welding atmosphere above 0.2% would produce hot cracking. Nitrogen was added to these atmospheres over the range 0.05% to 10%. The welding data are given in Table XXIV. These data show that if sufficient nitrogen is added to oxygen bearing argon atmospheres the hot center bead cracking normally noted will be eliminated. Typical welds made in these tests are shown with their X-ray pictures in Figs. 63-68. There is a marked change in the welds as the nitrogen concentration in the atmosphere is altered.

TABLE XXIV

DATA FOR WELDING WITH BOTH NITROGEN AND OXYGEN ADDED TO THE ARGON WELDING ATMOSPHERES

Sample	Atmosphere Additions % O_2	N_2	Welding Current	Welding Voltage	Arc Travel Speed In./Min	Comments
N-O-1	0.2	0.2	180	13.5	5.9	Center bead crack.
N-O-2	0.2	0.4	180	13.5	5.9	Center bead crack. Cross crack.
N-O-3	0.2	0.8	173	14.0	5.9	Center bead crack, first half.
N-O-4	0.2	2.0	175	13.5	5.9	Same as N-O-3 with cross crack.
N-O-5	0.2	5.0	175	14.5	5.9	No cracks. Bead wanders slightly.
N-O-6	0.4	0.4	180	14.0	5.9	Cracked full length.
N-O-7	0.4	0.8	180	14.0	5.9	Cracked full length.
N-O-8	0.4	2.0	180	14.0	5.9	Cracked full length.
N-O-9	0.4	5.0	180	14.0	5.9	Center bead crack.
N-O-11	0.4	7.5	175	15.0	5.9	No cracks.
N-O-10	0.4	10.0	175	15.0	5.9	Crater crack. No center bead crack.
N-O-12	0.2	0.1	200	14.0	5.9	No crack in weld.
N-O-13	0.3	0.1	200	15.0	5.9	Center bead crack.
N-O-14	0.3	0.3	227	15.0	5.9	Center bead crack. Crater crack. Melted through in one spot.

Sample N-O-1, Fig. 63, shows combined cross and center cracks. In Sample N-O-3, Fig. 64, only slight center cracking is observed, while Sample N-O-5, Fig. 65, shows a tendency toward cross cracking. Typical pictures of Samples N-O-6 to 11, Figs. 66-68, 0.4% O_2, show the same trend without the tendency to cross crack.

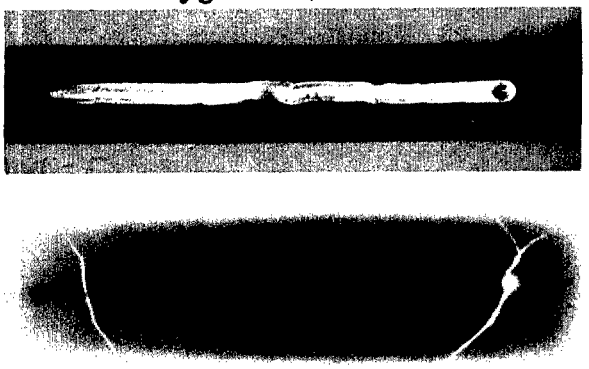


R 12788

Fig. 63 - Weld N-O-1, Welding Atmosphere Nitrogen 0.2%, Oxygen 0.2%.

R 12778

Fig. 64 - Weld N-O-3, Welding Atmosphere Nitrogen 0.8%, Oxygen 0.2%.



R 12780

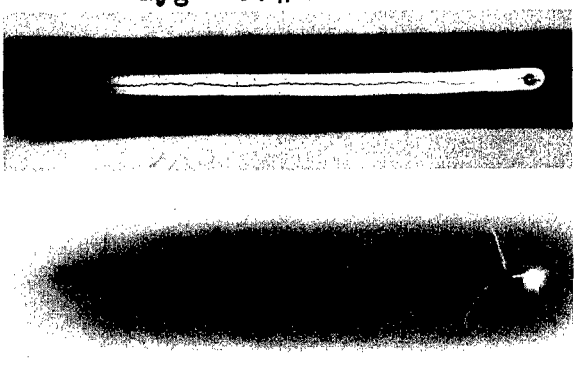
Fig. 65 - Weld N-O-5, Welding Atmosphere Nitrogen 5.0%, Oxygen 0.2%.

R 12782

Fig. 66 - Weld N-O-6, Welding Atmosphere Nitrogen 0.4%, Oxygen 0.4%.

R 12786

Fig. 67 - Weld N-O-11, Welding Atmosphere Nitrogen 7.5%, Oxygen 0.4%.



R 12787

Fig. 68 - Weld N-O-10, Welding Atmosphere Nitrogen 10.0%, Oxygen 0.4%.

TABLE XXV

WELDS MADE IN ARC-CAST CARBON DEOXIDIZED MOLYBDENUM UNDER ARGON-NITROGEN-OXYGEN ATMOSPHERES

Sample	Argon Atmosphere Addition		Weld Bead Analysis		Comments
	O_2	N_2	O_2	N_2	
N-O-1	0.2%	0.2%	-	.036	Center bead crack.
N-O-2	0.2	0.4	-	.042	Center bead and cross crack.
N-O-3	0.2	0.8	-	.023	Center bead crack first half.
N-O-4	0.2	2.0	-	.008	Center bead crack first half, cross crack.
N-O-5	0.2	5.0	.0081	.022	No cracks.
N-O-6	0.4	0.4	-	.025	Center bead crack.
N-O-7	0.4	0.8	-	.020	Center bead crack.
N-O-8	0.4	2.0	-	.022	Center bead crack.
N-O-9	0.4	5.0	-	.032	Center bead crack.
N-O-11	0.4	7.5	.0072	.029	No cracks.
N-O-10	0.4	10.0	.0104	.042	No center crack, crater crack.
N-O-14	0.3	0.1	.012	.010	Center bead crack, crater crack.

Samples N-O-10 and 11, 10% and 7.5% N_2, Figs. 67 and 68, both show crater cracks.

Severe oxidization of the iron electrode-holding collet over which the atmosphere passed suggested that this collet might be acting as a crude getter and reducing the amount of available oxygen near the arc. It was thought that if the temperature of the collet was increased by increasing the welding current in the absence of nitrogen, the collet could by its gettering action reduce the oxygen and prevent hot cracking. Weld samples N-O-12 to N-O-14 were made to check this point, Table XXIV. Sample N-O-12 was made using 200 amperes welding current and 0.2% O_2. No center bead cracking was observed. Sample N-O-13 was made with 0.3% O_2, using 200 amperes. Center cracking occurred in this sample. Weld N-O-14 used 0.3% O_2 and 227 amperes welding current. Center bead cracking was also observed in this sample. The cracking scatter in these three welds is approximately the same as was found previously with oxygen additions of 0.2 and 0.3%. Occasionally center bead cracking did not occur with 0.2% oxygen so that the lack of failure of Sample N-O-12 may have been of a statistical nature.

The weld beads made in nitrogen-oxygen-argon atmospheres were analyzed for nitrogen and oxygen when there was sufficient material to take a sample. These data are shown in Table XXV. The nitrogen content of the weld beads

is given as a function of the nitrogen and oxygen in the atmosphere, Fig. 69. These curves suggest an interaction between nitrogen and oxygen during welding. It appears that for certain oxygen and nitrogen combinations a minimum amount of nitrogen will be acquired by the bead. A three-dimensional view of these data indicates a complex surface with a low point near 2% nitrogen and 0.2% oxygen, or a nitrogen/oxygen ratio of 10:1. Examination of the curve for 0.4% oxygen in the atmosphere shows that the ratio of nitrogen to oxygen is 2:1 at the inflection point. The ratio for individual curves does not appear helpful but the low point for the surface shows a 10:1 ratio. However, it is possible that if some undefined ratio is used at oxygen concentrations in the order of 0.01%, both oxygen and nitrogen in the weld could be minimized. Improvement of weld quality by this means seems doubtful.

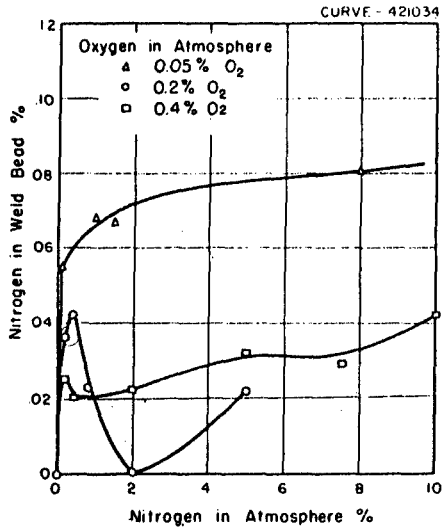
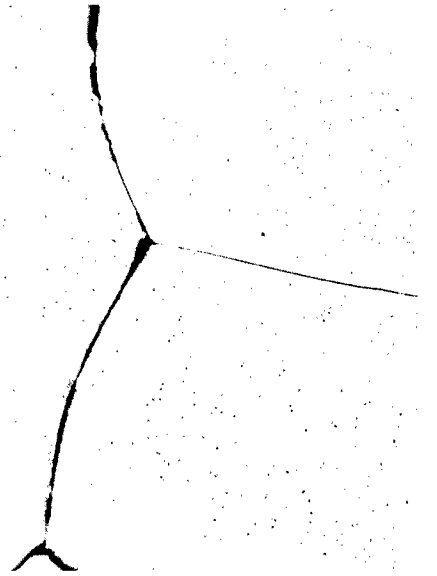


Fig. 69 - Nitrogen Acquired by Weld Bead as a Function of Nitrogen and Oxygen in the Welding Atmosphere.

The relationship between the oxygen in the welding atmosphere and oxygen in the weld bead for several nitrogen concentrations in the welding atmosphere was shown in Fig. 39. Unfortunately, samples with 0.02% oxygen and less than 5% nitrogen were not available for oxygen analysis because of cracks in the samples. The same condition was true for the samples made with 0.4% oxygen with less than 7.5% nitrogen. A complete set of data for N_2 = 0.1% was available and is shown with the other data in Fig. 39. The oxygen in the bead rises with the oxygen in the atmosphere in a nearly parabolic manner. Data were not obtained above 0.3% oxygen in the atmospheres because hot cracking made it impossible to obtain samples for oxygen analysis. Hot cracking occurs at oxygen contents above 0.012% in the weld bead. Included in Fig. 39 are points for 5% N_2, 0.2% O_2; 7.5% N_2, 0.4% O_2; and 10% N_2, 0.4% O_2. Assuming that all the curves are similar to the parabolic curve for less than 0.1% N_2, the dotted curves will be valid. From a three-dimensional consideration of these data, it appears that for a given

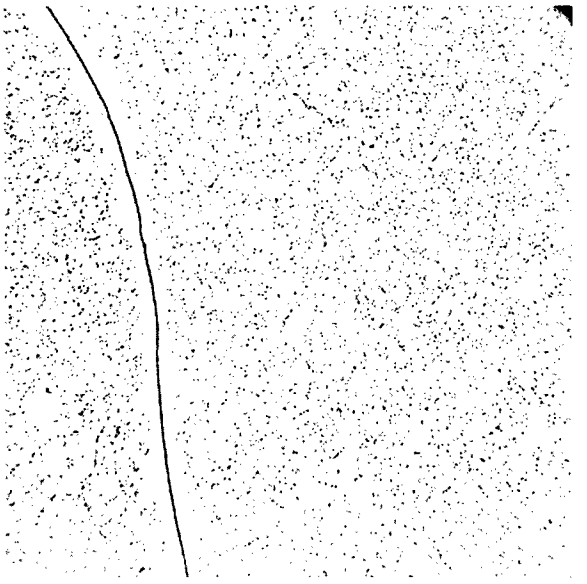
P54-49-5

Fig. 70 - Weld Made Under
0.4% O_2, 0.4% N_2,
Balance Argon, N-0-6
300X



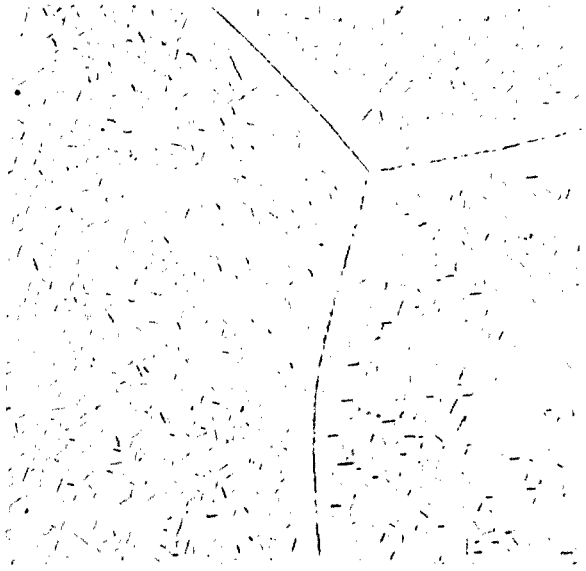
P54-49-1

Fig. 71 - Weld Made Under
0.4% O_2, 0.8% N_2,
Balance Argon, N-0-7
300X



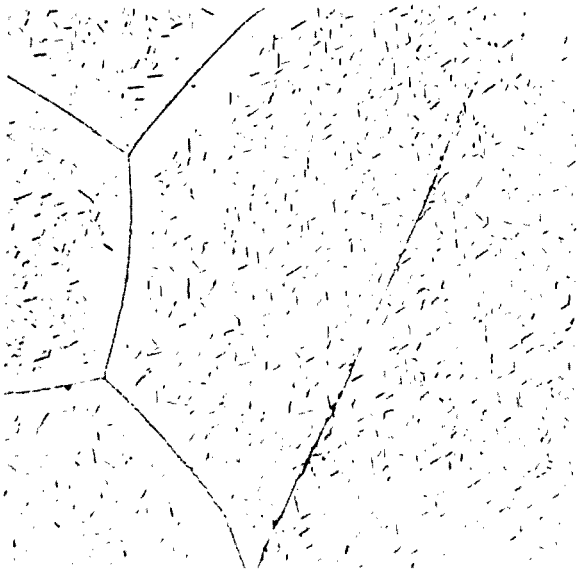
P54-37-9

Fig. 72 - Weld Made Under
0.4% O_2, 2.0% N_2,
Balance Argon, N-0-8
300X



P54-37-10

Fig. 73a - Weld Made Under
0.4% O_2, 5% N_2,
Balance Argon, N-0-9
Sound Zone 300X



P54-37-11

Fig. 73b - Weld Made Under
0.4% O_2, 5.0% N_2,
Balance Argon, N-0-9
Cracked Zone 300X

P54-37-13

Fig. 74a - Weld Made Under
0.4% O_2, 7.5% N_2,
Balance Argon, N-0-11
Region of Major Cracks
300X

P54-37-14

Fig. 74b - Weld Made Under
0.4% O_2, 7.5% N_2,
Balance Argon, N-0-11
Crack Source
300X

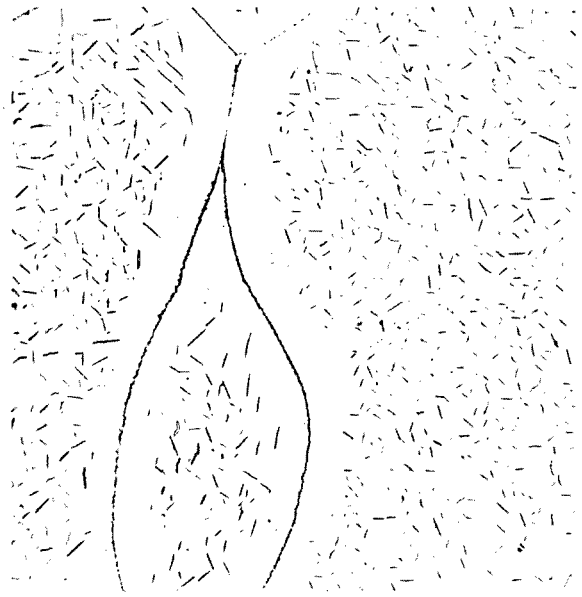


Fig. 75 - Weld Made Under 0.4% O_2, 10% N_2, Balance Argon, N-O-10 Sound Weld 300X

oxygen content there exists a nitrogen concentration which will give a minimum oxygen pickup in the weld bead. This suggests that the oxygen acquired by the material during welding may be reduced by nitrogen additions to the welding atmosphere. Unfortunately, the amount of nitrogen required to reduce the oxygen to useful limits, 0.004%, would produce excessive nitrogen in the weld bead.

The effect of changes of the nitrogen concentration on the microstructure of the weld beads made under nitrogen-oxygen-argon atmospheres is demonstrated in Figs. 70-75. Fig. 71 shows a boundary failure due to oxygen. The shape of the precipitate particles suggests oxide rather than nitrides. A similar condition with the beginning of a shift from boundary to transgranular fracture is shown in Fig. 73b. In Figs. 73-75, heavy precipitation becomes evident. The precipitate particles appear to be nitrides, however, the chemical analyses of these samples do not indicate a heavy nitride precipitate. It may be that oxygen influences the ability of molybdenum to form nitrides in a way similar to that which has been found in iron. It is important to note that when the nitrides appeared grain boundary cracking was no longer in evidence.

Photomicrographs of welds made using 0.4% oxygen and 0.4 to 10% nitrogen in argon atmospheres were shown in Figs. 70-75. As the nitrogen increases from 0.4 to 2%, Figs. 70-72, the amount of precipitate increases, however, the precipitate particles are spherical and do not have the needlelike nitride structure. Figs. 73a and b with 5% nitrogen show a typical nitride structure. This sample was cracked, Table XXV. Fig. 73b shows a zone near the fracture. The intergranular areas present near the right edge of this picture are not shown but a transgranular fracture plane is shown here. The transcrystalline crack follows one of the habit planes of the precipitate. This suggests

dislocation blocking and crack development parallel to the blocking particles.[15] The samples made with 7.5% nitrogen, Figs. 74a and b, show a similar condition. These photomicrographs suggest that as the nitrogen is increased the tendency toward transcrystalline fracture increases. However, it must be remembered that the origin of the fracture need not be transcrystalline for local transcrystalline fracture to occur. Very large nitrides are visible in Fig. 75. This sample was welded under an atmosphere of 0.4% O_2 and 10% N_2. There was no evidence of any form of cracking in this specimen. This indicates that the fracture origins of the cracks in the prior samples, Fig. 70 to 74, were probably intergranular. It must be emphasized that the samples in Figs. 70 to 74 are of as-welded samples subject only to welding thermal stresses. Thus it is probable that all the fractures shown occurred while the material was hot or as a result of thermal stresses produced during cooling.

Bend specimens were prepared from the sound portion of welds made in nitrogen-oxygen-argon atmospheres. These specimens were tested in bending and the data are given in Table XXVI. The relationship between bend deflection and test temperature is given in Fig. 76. These data show the combined effect of nitrogen and oxygen upon the bend ductility of molybdenum weld beads. In comparison with the results obtained when 0.2% oxygen was added to the argon, Fig. 35, Sample G9, the ductility of the samples made with both oxygen and nitrogen additions was better than expected. The sample with only 0.2% oxygen showed 0.05" deflection at 500°F while the sample welded with 0.2% O_2 and 0.8% N_2 showed 0.5" deflection at 300°F. Samples welded with 0.4% oxygen and 7.5 and 10% nitrogen, respectively, deflected 0.5" at 400°F while samples welded with 0.4% oxygen with no nitrogen additions were cracked as welded It appears from these data that oxygen and nitrogen in combination reduce the deleterious effects of each other when they are used in the proper ratio in the welding atmosphere. However, from the data shown in Fig. 76, oxygen-nitrogen-argon atmospheres have not been found which improve the ductility of the weld metal over that found in welds made using argon with a minimum of contaminating gases.

The effect of oxygen-nitrogen-argon atmosphere combinations upon the temperature of completely brittle behavior is shown at the lower end of the temperature deflection curve, Fig. 76. These data show that there is an increase in the temperature of completely brittle failure with increased

TABLE XXVI

BEND TEST DATA FOR WELDS MADE IN ARC-CAST CARBON DEOXIDIZED MOLYBDENUM UNDER NITROGEN-OXYGEN-ARGON ATMOSPHERES

Sample	Atmos. Comp. N_2	O_2	Test Temp.°F	Specimen Thickness	Width	Load In Pounds Prop. Limit	Max.	Fracture	Stress at Prop. Limit**	Deflection Inches
N-O-3	0.8%	0.2%	320	.0535	.253	13.5	40.8	-	28300	.500*
			240	.0535	.253	17	44	36.8	35600	.382
			160	.0535	.253	33	-	40.5	69200	.057
			80	.0535	.253	43	-	65	90200	.090
			-40	.0535	.253	70	-	83	147000	.021
			-100	.0535	.252	-	-	53	111000	.000
N-O-4	2.0%	0.2%	400	.061	.2495	20	57	-	32200	.500*
			360	.061	.2495	18.5	59	-	29800	.500*
			320	.061	.2495	15.5	56.2	50.5	25000	.349
			320	.061	.2495	22	-	65.3	33900	.151
			240	.061	.249	32	-	59.3	51600	.175
			80	.061	.249	59	-	74	95200	.039
			0	.061	.2495	-	-	62.8	101600	.000
			-40	.061	.2495	-	-	84	135000	.000
N-O-5	5.0%	0.2%	480	.0605	.249	17.5	57	-	28200	.500*
			440	.0605	.249	18.8	54.5	-	30400	.500*
			400	.061	.249	19	58.3	55.8	30600	.276*
			320	.061	.249	25	-	63.2	44000	.151
			160	.0605	.249	44	-	63	71000	.057
			80	.0605	.249	59	-	79	95200	.049
			-40	.0605	.249	88.7	-	103	143000	.015
			-80	.0605	.249	-	-	48.5	78300	.000
N-O-11	7.5%	0.4%	400	.059	.251	17	58	-	28400	.500*
			400	.060	.251	22	59	57	36600	.256
			360	.060	.251	19	60.2	50	31600	.348
			320	.060	.2515	23.8	62.2	41.2	39700	.443
			240	.060	.2515	37	-	63	61700	.148
			80	.060	.252	64.5	-	78	108000	.024
			0	.059	.251	-	-	75.2	126000	.000
N-O-10	10%	0.4%	480	.059	.252	18.5	59	-	31800	.500*
			400	.059	.252	17	60	47	29300	.379
			320	.059	.252	18	61.2	59.8	31000	.234
			240	.0595	.252	36	-	60	62000	.092
			80	.0595	.252	63	-	72	108500	.005
			40	.059	.2515	67	-	72.3	117000	.002
			0	.059	.2505	-	-	63.5	109300	.000

* No fracture.

** $\sigma = \frac{6P}{h^2}$ P = Load, h = Thickness. From equation $3/2\ P\ell^2/bh^2$ where $\ell = 1$ and $b = 0.250$

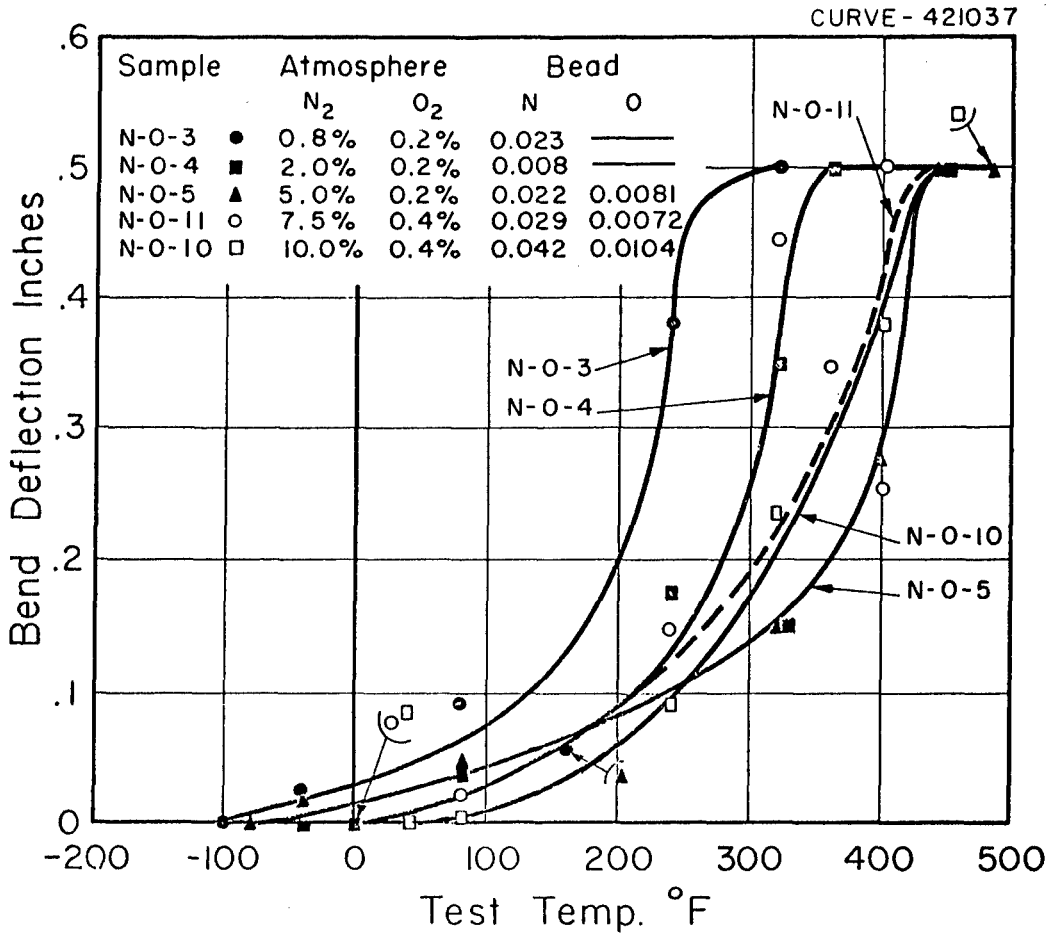


Fig. 76 - Relationship Between Test Temperature and Bend Deflection for Welds Made in Oxygen-Nitrogen-Argon Atmospheres.

amounts of oxygen and nitrogen in the argon. However, the effect is not as great as would have been expected. Nitrogen and oxygen tend to counteract each other in this temperature range. It is possible that nitrogen acts as a deoxidizer. Thus, the combined effects of nitrogen and oxygen on the weld ductility would be smaller than indicated by data obtained using separate additions of nitrogen or oxygen.

The calculated stress at the proportional limit is related to the test temperature for welds made in argon-oxygen-nitrogen atmospheres, Fig. 77. The stress at the proportional limit values for samples N-O-11 and N-O-10, 0.4% oxygen with 7.5 and 10% nitrogen, respectively, starts to rise at a slightly higher temperature which would appear as a reduction in ductility. In all samples except N-O-4, 0.2% O_2, 2.0% N_2,

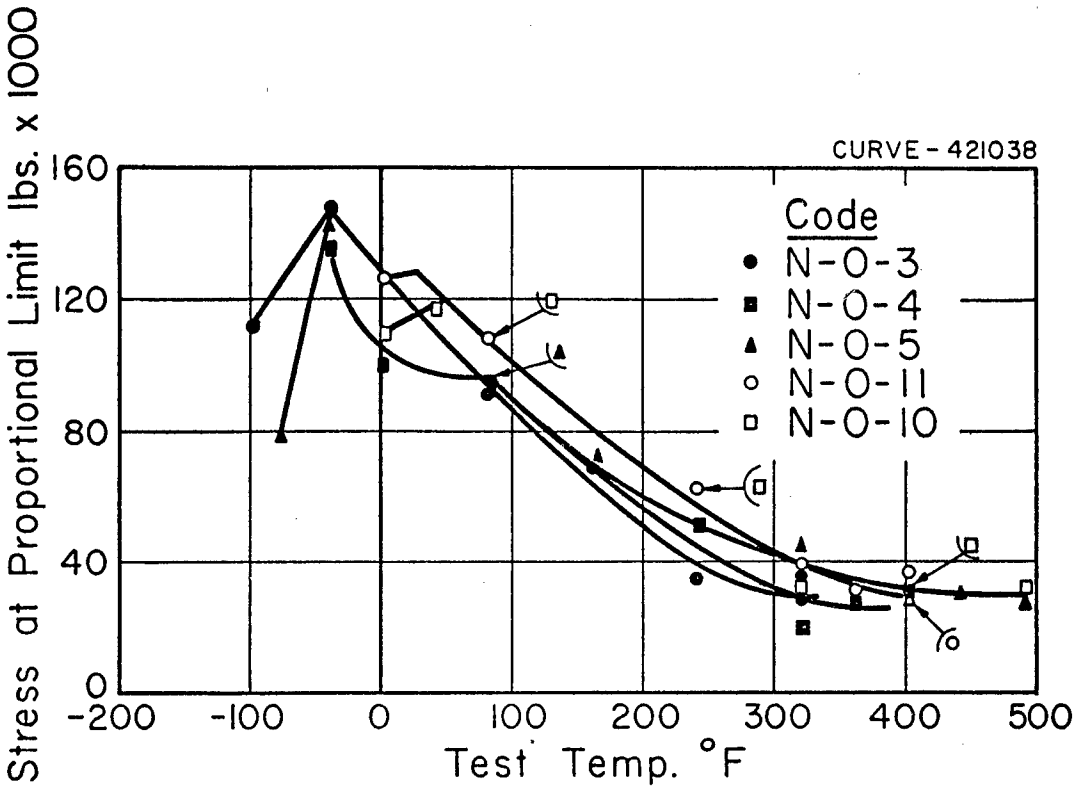


Fig. 77 - Relationship Between Test Temperature and Stress at Proportional Limit; Welds in Nitrogen-Oxygen-Argon Atmospheres.

the fracture strength dropped at temperatures below the initial brittle fracture temperature. No definite explanation is seen for this exception at present. A comparison of Fig. 77 with a previously obtained load at proportional limit curve, Fig. 43, shows that the welds made under nitrogen-oxygen-argon atmospheres increase in yield strength at a higher temperature, which indicates reduced low temperature ductility. The stress at the temperature of completely brittle failure is below the 165,000 psi value found for the best argon welding atmospheres available to date. However, for similar oxygen contents, 0.2%, in the welding atmosphere, the brittle fracture strength was found to be 90,000 psi in the absence of nitrogen additions. The effect of nitrogen additions was shown previously to be inactive below 0.07% in the weld metal. All of the samples welded with nitrogen-oxygen-argon atmosphere contained less than 0.04% N_2[6] so that

the principal drop in strength is due to oxygen. Any improvement in the strength at brittle failure along the proportional limit curve is due to nitrogen overcoming the deleterious effects of oxygen.

The preceding data indicate that nitrogen reacts with oxygen in the presence of the welding arc so that part of the oxygen is removed. The reaction probably results in the formation of one of the oxides of nitrogen, either NO or N_2O. The oxide would be swept away by the passage of gas over the weld in the chamber used, since the gas flow is 27.3 cu ft/hr. Formation and removal of oxides of nitrogen would explain the reduction below expected limits of oxygen and nitrogen in the weld bead when oxygen and nitrogen are present in the argon atmosphere.

Apparently when nitrogen is added to the atmosphere the reduction of hot cracking due to oxygen is the result of deoxidization by means of the nitrogen addition. The nitrogen is in the atomic state in the presence of the welding arc. The oxygen could also be atomic hence an easy reaction toward NO or N_2O. This condition suggests the possibility of using some other gas as a deoxidizer during welding. Hydrogen has some possibilities but the stability of water at arc temperatures may make its use impractical.

VI WELDS IN ALUMINUM DEOXIDIZED ARC-CAST MOLYBDENUM

The work with carbon deoxidized molybdenum in nitrogen atmospheres suggested that better results might be obtained if welds were made in molybdenum deoxidized with a material other than carbon. One lot of aluminum deoxidized arc-cast molybdenum was obtained from the Climax Molybdenum Company and reduced to sheet 0.065 in. thick using the procedures described in the first annual report, "Joining Molybdenum."[5] Three test welds were made in this material, Table XXVII. It was thought that cracks which occurred in the first sample might have been due to the prior cleaning in a salt bath process. However, cleaning did not cause the difficulty, and the cracking is believed to be due to a leak in the welding chamber. A photograph of weld Al 2 is shown in Fig. 78. The cross cracks in the area of the weld crater are not too promising, however, these may be the result of atmosphere deficiencies not detected by the gas analysis. A photomicrograph of the weld area in one of the welds, Fig. 79,

TABLE XXVII

WELDING DATA FOR WELDS MADE IN ARC-CAST ALUMINUM DEOXIDIZED MOLYBDENUM

Sample	Atmosphere N_2	Atmosphere O_2	Atmosphere Balance	Weld Current Amp	Weld Voltage	Arc Travel Speed In./Min	Comments
Al 1	Air Leak in Sample or Chamber		He	170	15	6	Center bead chevron cracks and cross cracks. Heavy film on sample. Sample as cleaned in salt bath.
Al 2	.15	<0.02	Argon	175	14	6	Crater and cross crack. Oxide around bead sample blasted prior to welding.
Al 3	.06	<0.02	Argon	180	14	6	Crater and cross crack. Sample as cleaned in salt baths.

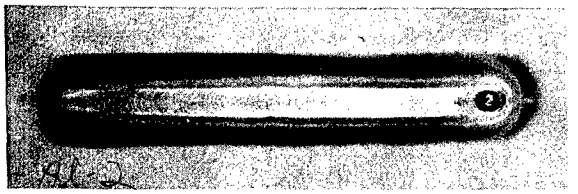


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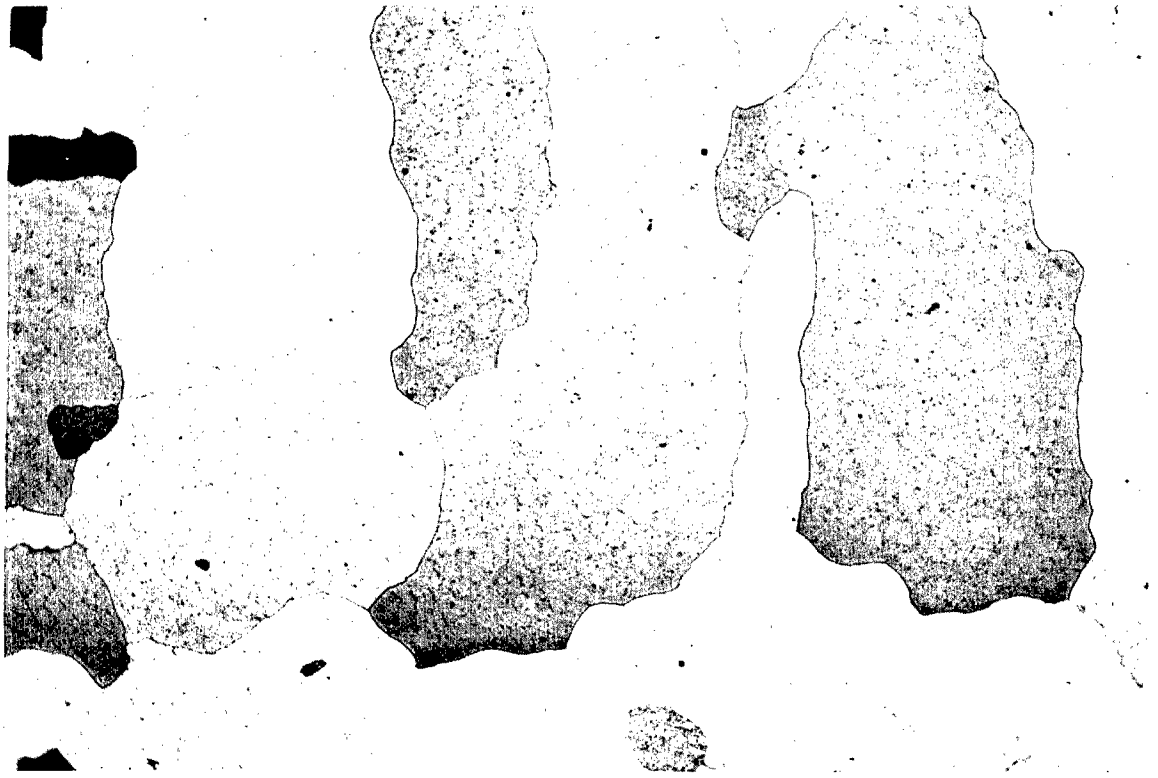
Fig. 78 - Weld in Arc-Cast Aluminum Deoxidized Molybdenum, Al-2

showed the usual large grain size but there is evidence of a high degree of polygonization. In comparison with some of the polygonized structures observed in other molybdenum weld beads this structure is very fine. It is possible that polygonization of the weld metal may aid in the properties by producing an effect similar to reducing grain size. Unfortunately, mechanical test data are not yet available for these samples. It is believed that the aluminum deoxidized molybdenum should be investigated further to determine its properties.

VII PRE-STRAINING OF WELD SAMPLES

Work by Bechtold[1] has shown that the ductility of molybdenum is improved by the introduction of cold deformation at temperatures where the



P54-144-1

Fig. 79 - Weld Zone in Arc-Cast Aluminum Deoxidized Molybdenum Showing Evidence of Polygonization. 100X

material is ductile. It was thought that the ductility of the cast weld beads could be improved if some cold deformation could be obtained in the weld metal. Prior experience had shown that the weld metal could sustain at least 8% plastic deformation at temperatures of 300°F. A group of weld beads was made in arc-cast carbon deoxidized plate under the best available argon atmosphere. These welds were examined by means of X-rays and found to be free of cracks and porosity. The welds were made using a welding current of 180 amperes and arc voltage of 14 volts and an arc travel speed of 6 in. per minute. The atmosphere consisted of argon with $<$0.02% oxygen and $<$0.1% nitrogen. These welds were cut into tensile test specimens with reduced sections at the weld and surface ground to clean up the weld area. All samples were ground to the same final thickness. The samples were strained in tension 0%, 4%, and 8% at 300°F. The strained samples were then reground to bend specimens. In all cases the weld location was maintained at the

center of the bend specimen and the upper surface of the weld was in the position of maximum tension in the bend test. These samples were tested in bending over a range of temperatures, Table XXVIII.

TABLE XXVIII

BEND TEST DATA FOR PRESTRAINED WELDS

Sample	Prior Deformation %	Test Temp. °F	Thickness Inches	Width Inches	Load at Proportional Limit	Stress at Proportional Limit	Maximum Deflection
G35-3	0	320	0.047	0.2515	Not Obtained		0.500*
2	0	160	0.047	0.252	11.7	31800	0.125
1	0	80	0.047	0.252	18.9	51400	0.145
4	0	-110	0.0465	0.251	56	152000	0.012
5	0	-160	0.047	0.2515	62	168500	0.002
6	0	-200	0.0465	0.252	69.2	188000	0.000
G38-1	4	320	0.048	0.249	14	36500	0.500*
3	4	240	0.048	0.249	19	49500	0.231
2	4	80	0.048	0.249	34	88600	0.088
5	4	- 80	0.047	0.249	21	54700	0.017
6	4	-160	0.048	0.249	45	117000	0.008
G39-3	8	320	0.047	0.236	15	44000	0.500*
4	8	240	0.046	0.236	17	49800	0.153
2	8	160	0.046	0.237	21	61500	0.129
1	8	80	0.047	0.237	28	82000	0.144
5	8	- 80	0.046	0.236	24	70300	0.008
7	8	-160	0.046	0.237	49	143500	0.011

*Maximum deflection, 100° bend angle, for fixture used.

The bend deflections as a function of temperature are shown in Fig. 80. There is no apparent difference in the strained and unstrained samples except at low temperatures. Below -80°F the bend deflection seems to be slightly better in the strained sample. Complete brittleness was attained at -160°F in the unstrained samples while the strained samples appeared to have a small amount of ductility at this temperature. Examination of the stress at the outer fiber at the elastic limit for the strained samples showed a change in the curve between 80 and -80°F, Fig. 81. At temperatures above 80°F, the stress at the proportional limit temperature curve rises more rapidly in the strained than in the unstrained specimens. However, between 80° and -80F this condition is changed and the stress at the proportional limit at -80°F is less than that found at 80°F. The rise in the

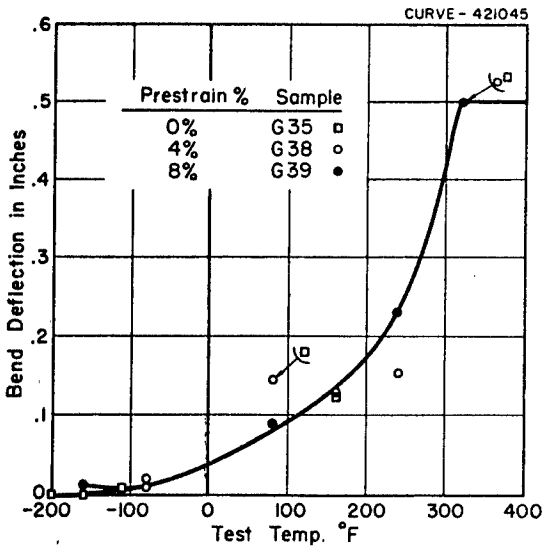


Fig. 80 - Relationship Between Bend Deflection and Temperature for Welds Prestrained at 300°F.

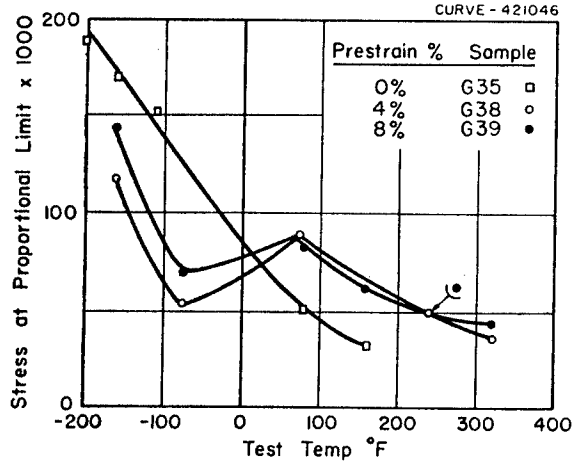


Fig. 81 - Relationship Between Test Temperature and Stress at Proportional Limit for Welds Prestrained at 300°F.

proportional limit below -80°F is more rapid in the case of the strained samples so that it appears that the proportional limits would be the same at -200°F. The reason for the shift in the proportional limit curves is not understood at this time and the test results should be rechecked to confirm these data. Further work in this direction is suggested. If the temperature at which the rise in the proportional limit occurs can be decreased, it may be possible to improve the molybdenum welds so that they have usable ductility at temperatures within the atmospheric range.

VIII IMPROVEMENT OF WELDING ATMOSPHERES

The data collected on oxygen and nitrogen additions to the welding atmosphere suggested that some means be found to improve the purity of the atmosphere. Some of the early work with the welding chamber used indicated that the iron collet used to hold the welding electrode was acting as a crude getter because all the gases entering the welding chamber passed over the collet which was heated by the arc. Titanium collets were tried with the hope of reducing the amount of oxygen and nitrogen in the incoming gas before it reached the weld puddle. Subsequent work showed this method to be only moderately successful. Further improvement of the welding atmosphere was

attempted by the use of helium. The level of nitrogen in helium is in general lower than can be attained in welding grade argon. The early tests with helium atmospheres were not too promising but later results suggest that this gas is worth careful consideration. Attempts have been made to further purify the argon and helium atmospheres used by means of gettering trains using hot titanium chips. These tests have met with moderate success.

Titanium Collets

Reference to Fig. 3 shows that the collet which holds the tungsten welding electrode has small slots through which all of the incoming gas must pass. During the welding operation this collet is heated by the arc. The passage of the welding atmosphere over the hot metal will permit the oxygen in the argon to react with the iron in the collet. This condition was first observed when sufficient oxide was produced on the iron collet during one weld to make it necessary to change the collet before the next weld was made. If the collet was not changed the welding arc in its search for oxygen would start from the collet instead of the electrode. In order to take full advantage of these phenomena, collets were made from titanium and two welds were made using welding grade argon. The welding data are given in Table XXIX. The composition of the welding atmosphere in the chamber before the arc was started is given, but it is not possible with the present equipment to sample the welding atmosphere under the welding arc. Both of the test welds were free of all forms of cracks and porosity.

The ability of the titanium collet to remove oxygen from the incoming gas can be estimated from the discoloration of the collet, Fig. 82. Metallographic examination of the weld zone gives a further indication of the gettering ability of the titanium collet. Fig. 83 shows the weld zone at the beginning and end of the weld. The action of the collet is at its peak when the collet is hot, and at the beginning of the weld the collet would be cold and ineffective. Examination of the photomicrographs, Fig. 83, shows that the fine precipitates in the grains of the sample taken at the beginning of the weld tend to have a needlelike shape indicating nitrides. However, the precipitates in the specimen from the end of the sample are

TABLE XXIX

WELDS MADE WITH TITANIUM WELD COLLETS

Sample	Atmosphere Before Welding	Current	Voltage	Arc Travel Speed Inches/Min	Comments
Ti-1	99.98 A Trace O_2 .02 N_2	180	13	5.9	No cracks; 70% penetration.
Ti-2	99.98 A Trace O_2 .02 N_2	210	13.5-14	5.9	No cracks; 90-100% penetration.

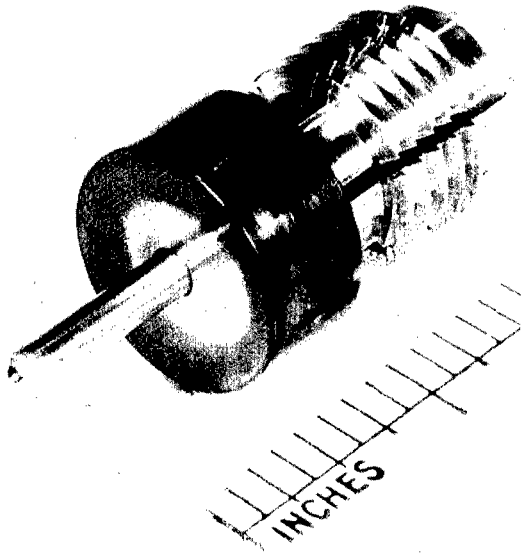


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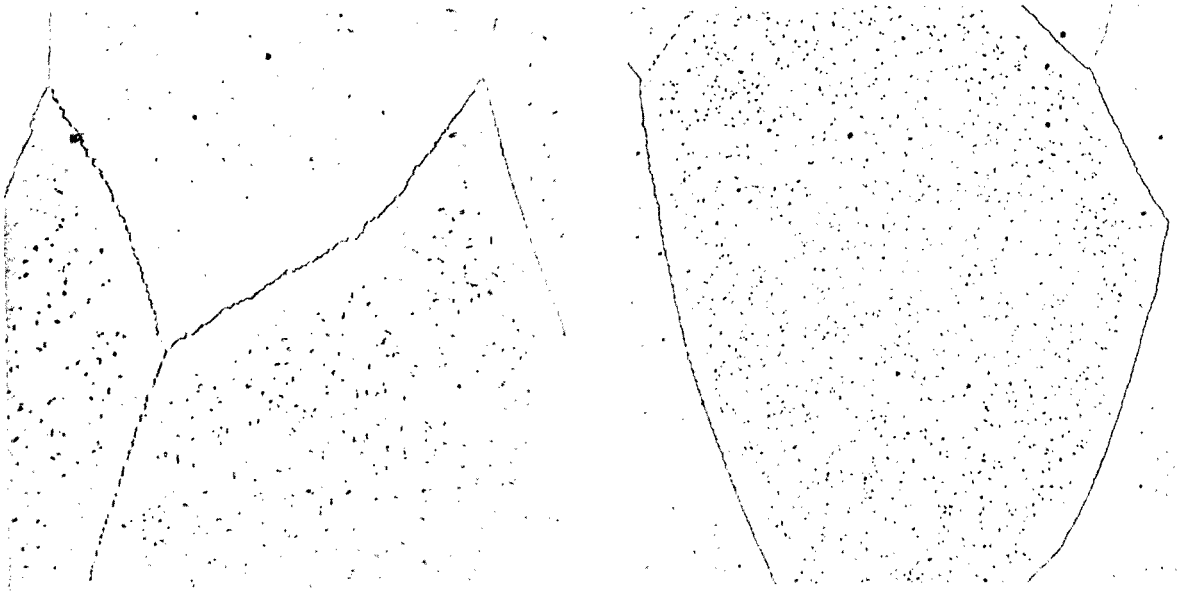
Fig. 82 - Titanium Weld Collet After Use on One Weld.

more nearly spheres, indicating carbides. In both cases the nature of the precipitate indicates some purification of the atmosphere. The presence of nitrides indicates that the gettering action had not started and their absence at the end of the weld indicates purification with respect to nitrogen. The carbides at the end of the weld and the absence of carbides at the beginning indicate a reduction in the oxygen in the atmosphere.

The welds made using the titanium collets were cut into bend specimens and tested over a range of temperatures. The test data are shown in Table XXX. Curves showing the bend deflection as a function of these temperatures are shown in Fig. 84. The relationship between the test temperature and the stress at the proportional limit is shown in Fig. 85. These data do not show any exceptional result with respect to the stress at the proportional limit or the bend deflection. However, the titanium collets successfully indicated the need for getters and atmosphere quality indicators directly over the welding arc. There is a definite indication that better getters should be tried.



(a) Beginning of Weld
P54-37-3 300X

(b) End of Weld
P54-37-5 300X

Fig. 83 - Weld Made in Arc-Cast Carbon Deoxidized Molybdenum, Argon Atmosphere, Trace O_2, 0.02% N_2, Titanium Collet. (Ti 1).

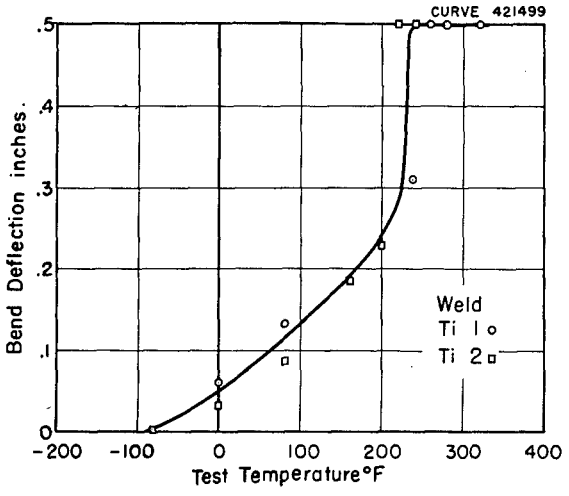


Fig. 84 - Bend Deflections vs. Test Temperature. Welds Made With Titanium Collets.

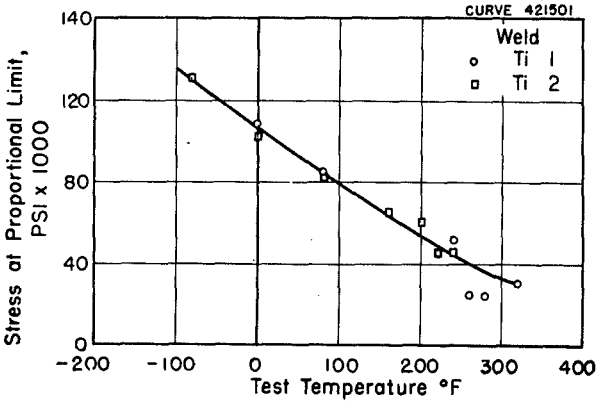


Fig. 85 - Stress at Proportional Limit as Function of Test Temperature for Welds Made With Titanium Collets.

TABLE XXX

BEND TEST DATA

WELDS MADE WITH TITANIUM COLLETS

Spec. No.	Test Temp. °F	Thickness Inches	Width Inches	Prop. Limit Load Lb	Prop. Limit Stress psi	Max. Load Lb	Load At Fracture Lb	Deflection Inches
Ti-1a	80	.0595	.250	51	85000	-	80.3	.133
b	240	.060	.250	31	51700	60	55.0	.311
c	320	.060	.250	19	31700	51	----	No Fracture
d	280	.060	.250	15	25000	52.2	----	No Fracture
e	260	.0595	.250	15	25000	51	----	No Fracture
f	0	.0595	.250	66	108500	-	92	.063
Ti-2a	80	.061	.247	50	83500	-	77.5	.077
b	240	.060	.247	28	46700	57.2	----	No Fracture
c	160	.061	.247	40	66700	64	63.5	.186
d	200	.060	.247	37	61700	59.8	58.3	.230
e	220	.060	.247	28	46600	58.2	----	No Fracture
f	0	.0605	.247	62	103500	----	87	.035
g	- 80	.061	.247	81	131500	----	96	.003

Helium Atmospheres

The nitrogen level in commercial helium is often lower than that found in welding grade argon according to the analysis data furnished to the suppliers by the U.S. Bureau of Mines. However, this analysis may vary because of variations in the methods of filling commercial tanks. Three weld beads were made using

TABLE XXXI

WELDING DATA FOR WELDS MADE IN HELIUM

Sample	Welding Atmosphere N_2	Welding Atmosphere O_2	Gettering Train	Current Amp	Voltage	Arc Travel Speed In./Min	Comments
He 1	<0.05%	Not Detected	None	Recorder Failure	15.5	6	Bright weld, crater crack, wide bead, 100% penetration, blue haze on surface.
He 2	0.6	Not Detected	Hot Ti Chips 1500°F	200	17.5	6	Wide bead film on surface, no cracks.
He 3	0.6	Not Detected	Hot Ti Chips 1500°F	200	17-21	6	Wide bead with crater crack. Distortion caused voltage to shift.

TABLE XXXII

BEND TEST DATA FOR WELD MADE IN HELIUM ATMOSPHERE

Sample	Test Temp. °F	Thickness Inches	Width Inches	Load in Lb Prop.Limit	Load in Lb Maximum	Load in Lb Fracture	Stress at Prop.Limit psi	Bend Def. In.
He-1-8	-280	0.056	0.250	-	-	103	197000	0.000
7	-240	0.056	0.251	105	-	114	201000	0.001
6	-160	0.056	0.250	90	-	107	172000	0.009
5	- 80	0.056	0.250	80	-	89	153000	0.007
1	80	0.056	0.250	46	-	70.5	88000	0.171
4	160	0.056	0.250	36	52.5	-	68900	No Fracture
3	240	0.055	0.250	25.5	45	-	48700	No Fracture
2	240	0.055	0.250	26	44	37	49700	0.424

commercial helium. The welding data, given in Table XXXI, show crater cracks in two of the three welds. These results were not considered promising and only a few tests were made on the weld metal. Weld He 1 was tested over a range of temperatures. The results of these tests were better than was expected on the

basis of the visual and X-ray inspection. The bend test data are given in Table XXXII. The bend deflection and the stress at the proportional limit are given as a function of the test temperature in Fig. 86. While the bend deflection curve did not show exceptional results, the temperature for 0.4 in. deflection was 160°F which is better than was obtained with any of the argon atmospheres used previously. It is believed that a higher purity helium will make possible further reductions in the temperature required for 0.4 in. deflection. The stress at the proportional limit curve, Fig. 86, shows the maximum value obtained for the proportional limit 201,000 psi at the temperature for completely brittle failure (-280°F). Previously, the upper limit of the proportional limit was 190,000 psi.

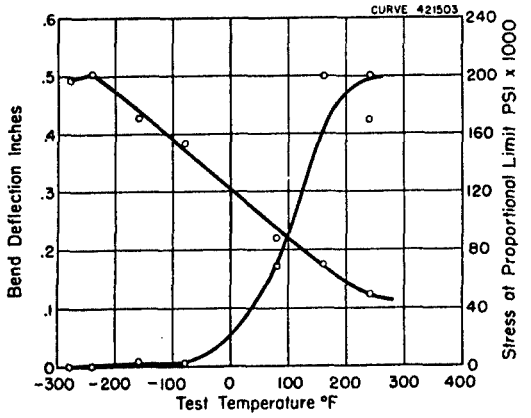


Fig. 86 - Bend Deflection and Proportional Limit as Related to the Test Temperature. Weld Made in Helium.

A metallographic sample of the weld made in helium shows the center of the weld zone, Fig. 87. There is definite evidence of polygonization in the large grains in this area. Apparently the weld zone was subject to bending while at elevated temperatures. It may be possible to use this condition to give the effect of reduced grain size. The ability of the subgrain boundaries to remove the impurities from the main boundaries should be investigated.

An analysis was made of one of the welds made under helium atmospheres. This weld was made using commercial helium which had been passed over hot titanium chips at 1500°F prior to entering the welding chamber. The nitrogen in the sample was 0.003% which is very close to the analysis of the unwelded plate, 0.002%. Unfortunately, the analysis for oxygen was not completed and physical test data are not available on this sample. However, on the basis of nitrogen data shown earlier in this report, it is believed that these welds show improved ductility. Further investigations of welds made in purified helium are in order.

Fig. 87 - Weld Zone of Sample Welded in Helium - 100X - P54-144-2

Purified Argon

Two welds were made in argon which had been passed over hot titanium chips prior to entering the welding chamber. These welds were free from defects except for one crater crack. Physical test data are not available on these samples at present. Purification of argon should be investigated as well as purified helium.

IX HEAT TREATMENT OF WELDS

Only a limited amount of investigation has been done in connection with the effect of heat treatment on the properties of weld metal in molybdenum. One weld was stress relieved at 900°C (1652°F) for four hours in vacuum. Bend test data were obtained for this sample over a range of temperatures, Table XXXIII. The relationship between bend

TABLE XXXIII

Bend Test data for sample weld in argon on arc-cast carbon deoxidized molybdenum, stress relieved two hours, 900°C vacuum.

Temp.	Thickness	Width	Load Prop. Limit Lb	Stress Prop. Limit psi	Deflection Inches
-160	.059	.251	94	162000	.001
- 80	.059	.251	74	127500	.018
0	.059	.251	64	11100	.047
160	.059	.251	34	58600	.142
240	.059	.251	23	39600	.319
280	.059	.251	29.5	50800	.500

deflection, stress at the proportional limit and the test temperature are given in Fig. 88. This weld metal was fused in an argon atmosphere with $< 0.05\%$ O_2 and $< 0.1\%$ N_2. The analysis of the weld bead after heat treatment shows the carbon to be 0.08% and the nitrogen 0.008%. The unwelded plate showed 0.003% N and 0.06% C. Other data given earlier in this report showed the expected nitrogen in the weld zone to be 0.02 to 0.05% for the welding atmosphere used. The change in the nitrogen concentration could be due to diffusion of the nitrogen to the surface and dissipation into the vacuum or diffusion into the low nitrogen portion of the base plate. The increase in the carbon content may be due to back diffusion of oil from the vacuum pump.

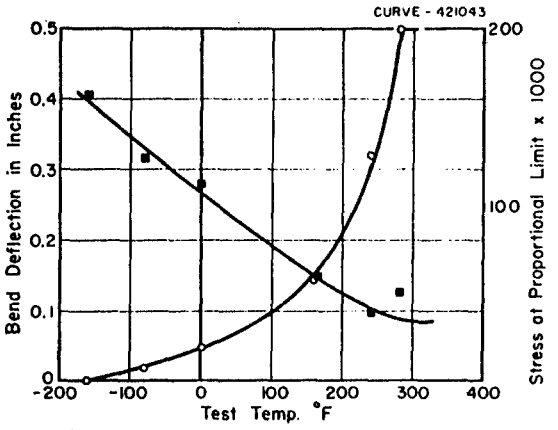


Fig. 88 - Physical Test Relationships for a Weld Stress Relieved 2 Hrs. 900°C in a Vacuum.

When the increase in the carbon is considered with respect to the decrease in the nitrogen for the stress relieved sample and the atomic percent of nitrogen and carbon is compared with the curves shown in Figs. 59 and 61, it will be seen that the temperature for 0.4 in. deflection

and brittle failure is in agreement with previous results. These points occur at 0.68 atomic % N + C at +270°F, and -160°F for ductile and brittle failure respectively. If this weld could have been made without the increase in carbon, the entire bend deflection curve would have been shifted to lower temperatures. These results suggest that carefully controlled welding atmospheres and material followed by a post-welding heat treatment could improve the weld ductility.

Fig. 89 - Weld Heated 2000°C 2 Hrs in Vacuum. Original Nitrogen 0.08%, After Heating N_2 0.04% P-54-97-8 300X

A second exploratory study was made of the effect of heat treatment on the nitrogen concentration in the weld bead. A small section was taken from a sample, G18, which had been welded in an atmosphere of 8% nitrogen and the balance argon. The weld in this case contained 0.081% N. The test sample was heated in a vacuum of 10^{-6} mm of Hg. at 2000°C for two hours. A chemical analysis for nitrogen was made and a metallographic specimen was taken. The nitrogen in the weld bead after heat treatment was 0.04%. This indicates diffusion either into the low nitrogen parent plate or to the surface of the plate followed by dissipation in the vacuum system. The analysis of the base plate after heat treatment has not yet been checked.

A metallographic specimen of the weld used in the 2000°C heat treatment prior to treatment was shown in Fig. 54. The heavy nitride precipitate in the grain matrix is characteristic of welds made in nitrogen bearing atmospheres. The section of this same weld bead after the heat treatment shows no evidence of nitrides in the grain matrix and a very heavy but discontinuous boundary precipitate, Fig. 89. This suggests the possibility that welds contaminated with nitrogen may be improved by diffusing some of the nitrogen from the weld zone and rendering the remaining nitrogen ineffective by the equivalent of an overaging process. The overaging process may make it

P54-59-1 100X
Fig. 90 - Surface of Weld Heat Treated 2 Hrs at 2000°C.

possible to reduce the rigidity of the grain matrix caused by the nitrides and reduce the effective dislocation blocking by coherent precipitates in the region of the grain boundary. This combination of events may improve the ductility of the material.

The surface appearance of the vacuum heat treated material is shown in Fig. 90. Prior to heat treatment the surface showed no unusual structure. The appearance was similar to that shown in the first annual report, WADC 54-17. Prior boundaries formed during welding may be seen in Fig. 90. The heavy surface veining appears to be confined to habit planes and the veins change with the orientation of the parent grain. Two types of veins are observed, one is sharp and distinct, the other has a featherlike appearance. It was thought that the latter type could be produced by the surface being nearly parallel to the vein. It is possible that these veins are due to some form of macroscopic slip which occurred during heat treatment. However, the exact nature of the phenomenon is not known.

In general, the heat treatment of welds in molybdenum seems to be promising. It is probable that the deleterious effects of nitrogen in the weld metal can be reduced either by diffusion from the weld zone or by overaging the precipitate in such a way as to render it ineffective with respect to plastic flow. In either case, further work on the heat treatment of weld metal should be undertaken.

X BUTT JOINTS

Several butt welds were made in carbon deoxidized arc-cast molybdenum sheets. Previous experience had shown that sheet laminations must be avoided

if joints are to be made. Therefore, all the test plates were carefully inspected prior to welding. The edges were also examined for rolling scale or other sources of oxygen. The plates were butted together and held in position with a copper hold-down plate. The weight of the hold-down plate, 4 lbs, was the only restraint. The welds were made in the chamber used for previous tests and welding grade argon was used as an atmosphere. Welding was done with a tungsten electrode and no filler metal was added. Welding data are given in Table XXXIV.

TABLE XXXIV

WELDING DATA FOR BUTT WELDS

Sample	Atmosphere O_2	Atmosphere N_2	Arc Current	Arc Voltage	Arc Travel In./Min	Fused Bead Comments
B6	0.05%	0.15%	200	13	6	No cracks; clean, bright weld.
B7	0.05	0.1	205	13.8	6	Melted through for 1 in. Remainder of weld good.

Some difficulty was experienced in properly locating the weld bead but this was an equipment limitation. The welds given in Table XXXIV were those on which the welding arc was centered along the joint for the entire joint length and 100% penetration was obtained. Some of the preliminary welds were rejected because of alignment and penetration difficulties.

A typical photograph and X-ray picture of butt weld B6 are shown in Fig. 91. Both welds B6 and B7 were free of cracks and porosity. Weld B7, however, did not join for its full length because it was not possible to change the electrode position and arc current rapidly during the weld. In Sample B7, the welding current was slightly too high causing the melted through area.

Metallographic examinations were made of the weld areas of butt welds B6 and B7. The weld edge showed evidence of very fine porosity not detectable by X-ray examination. Otherwise the weld showed typical fine precipitates which are believed to be nitrides and carbides. The grain boundaries showed evidence of a discontinuous boundary film in some locations. It appears that

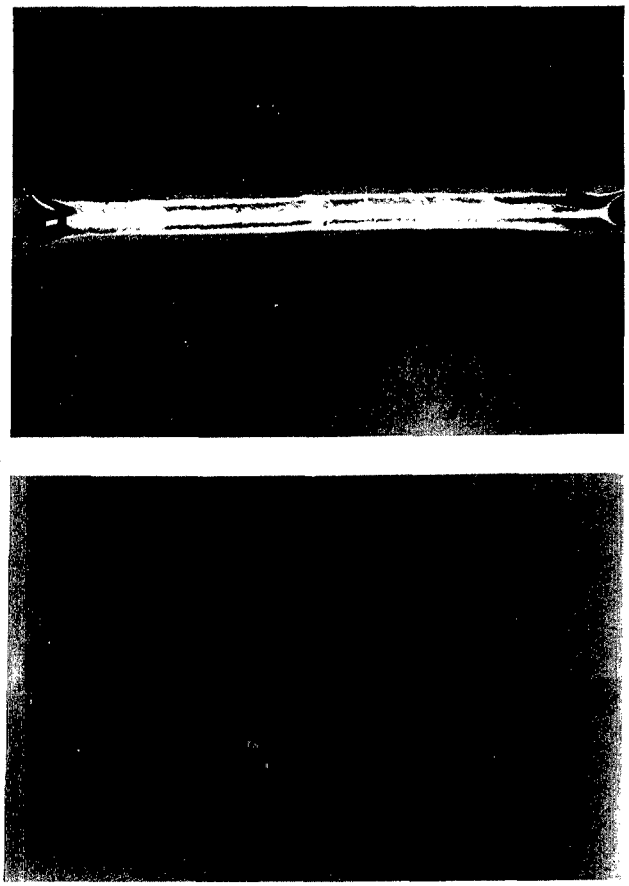


Fig. 91 - Butt Weld in Arc-Cast Carbon Deoxidized Molybdenum. R 13122

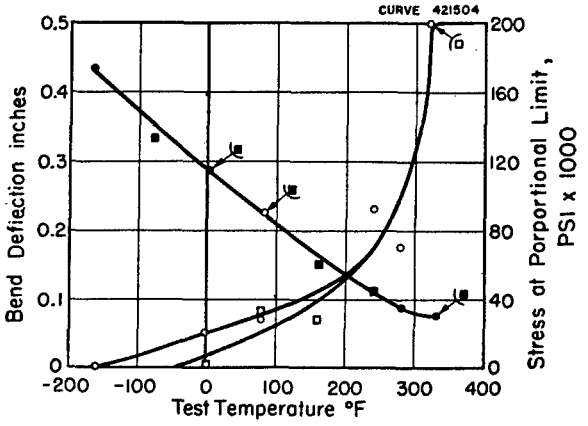


Fig. 92 - Relationship Between Bend Deflection, Stress at Proportional Limit and Test Temperature; for Butt Welds in Arc-Cast Carbon Deoxidized Molybdenum.

this weld was made within the satisfactory operational range of oxygen concentration in the bead as suggested in Fig. 42.

Welds B6 and B7 were cut into bend specimens. The temperature-bend deflection relationship is given in Fig. 92. The test data are given in Table XXXV. The bend deflection curves for both welds compare favorably with curves obtained for bead on plate welds reported earlier. The temperature for ductile behavior, 0.4 in. deflection, is about 100°F above the minimum previously obtained; however, this may be due to high nitrogen in the welding atmosphere, Table XXXIV. The temperature of completely brittle behavior falls between -50 and -160°F which is equivalent to welds shown earlier. The butt welds show a normal rise in the proportional limit as a function of decreasing temperature, Fig. 92. In general, it was concluded that the butt welds were as good as prior bead-on-plate welds.

TABLE XXXV

TEST DATA - BUTT WELDS IN ARC-CAST CARBON DEOXIDIZED MOLYBDENUM

Sample	Test Temp. °F	Thickness	Width	Load at Prop. Limit	Stress at Prop. Limit	Bend Deflection Inches
B6	-160	.056	.250	91	174000	.001
	0	"	"	60	115000	.055
	80	"	"	47	90000	.071
	240	"	"	23.5	45000	.229
	280	"	"	19	36400	.176
	320	"	"	16	30600	.500
B7	- 80	.056	.250	70	134000	.005
	0	"	"	60	115000	.004
	80	"	"	46	89000	.081
	160	"	"	32	61200	.071
	320	"	"	16	30600	.500

XI SUMMARY

The work on both sintered and arc-cast molybdenum has indicated that if certain welding and material conditions are carefully controlled, it will be possible to make joints having appreciable ductility. Molybdenum requires a deoxidizing agent regardless of its means of fabrication, sintered or arc cast. The nature and requirements of the deoxidizer have been established by work reported here. The deoxidizer must not only remove oxygen from the molybdenum but it must be nonvolatile at welding temperatures; it must not form grain boundary films nor be molten in the grain boundaries after the molybdenum has solidified. The products of deoxidization must either be removed during sintering or arc casting or be nonvolatile at welding temperatures. If the deoxidization products are not removed during fabrication, they must not be molten in the grain boundaries after the grains solidify nor can they form precipitates which interfere excessively with plastic deformation. With one exception the deoxidizing agents tried, C, Al, Ta, Nb, and Ti, have failed to meet one or more of these requirements. Titanium appears to meet all the requirements. It forms a nonvolatile oxide which is floated off during welding or remains as spheres and inhibits grain growth without complete boundary films. It does not volatilize

during welding and its oxide is stable. Since it is possible to obtain higher purity and more complete deoxidization with arc-cast molybdenum, it is recommended that future work be done with arc-cast material deoxidized with titanium or some other deoxidizer meeting the above requirements.

The welding atmosphere used to form joints in molybdenum must be very carefully controlled with respect to three elements, oxygen, nitrogen and carbon. The work in this report clearly indicates the harmful effect of these elements. Oxygen causes hot center bead cracking when present in the gaseous atmosphere in excess of 0.1% and crater cracks when in excess of 0.02%. Oxygen must be minimized in the weld by some means since it reduces the ductility when present in the weld metal in excess of 0.004% as compared to 0.0018% in the unwelded plate. Oxygen can be eliminated by prior purification of the atmosphere and careful selections of the material with regard to surface and sheet lamination. The data on the interaction of oxygen and nitrogen suggest that oxygen may be eliminated by reaction with a deoxidizing gas in the welding chamber. While nitrogen was shown to have a deoxidizing action, it has other harmful effects and different reducing gases such as hydrogen and chlorine might be more successful. With the atmospheres available at present, however, it is recommended that the oxygen level be maintained at less than the concentration shown in Fig. 42.

The effects of the interstitial elements, nitrogen and carbon, have been shown to be detrimental to the ductility of molybdenum welds. The data indicate that these elements should be eliminated as completely as possible. The material should have a minimum nitrogen and carbon content, and the welding atmosphere should also be free from these elements. Carbon may be eliminated from the material by deoxidization with titanium or another suitable deoxidizer. Nitrogen enters primarily from the welding atmosphere. The data indicate nitrogen may be eliminated by using helium of high purity or by further purification of helium prior to welding. It may be possible to accomplish this with argon but the amount of nitrogen to be removed is larger. Purification trains in the gas supply system may be an answer to elimination of nitrogen.

Nitrogen may be removed from the weld zone by heat treatment which involves diffusion of the nitrogen into the parent plate or the furnace atmosphere. Overaging of nitride particles may also be used to render nitrogen ineffective in reducing the ductility of molybdenum welds.

The data suggest that hydrocarbons in the atmosphere might cause trouble

and the welding atmosphere should also be free of these materials.

Post-weld straining of weld metal has shown some possibilities in lowering the temperature for the increase in the proportional limit as a function of temperature. The data are as yet inconclusive but further investigation would be wise. There is also a possibility that post-weld straining at elevated temperatures should be tried to take advantage of the polygonization phenomenon observed in many welds. The present data only involved post-weld straining at 300°F; much higher temperatures would be required for polygonization. Polygonization could have the effect of reducing the grain size, and since the effect of detrimental impurities in molybdenum is a function of the grain size, this possibility deserves consideration.

Butt joints shown in this report indicate that joints as well as bead-on-plate welds can be made having properties which are a function of the concentration of carbon, oxygen and nitrogen in the parent plate and welding atmosphere. Welded joint properties will then be as good as the material and welding media will permit. In brief, weld ductility in molybdenum should reach a maximum level when oxygen, carbon and nitrogen have been eliminated from the weld metal.

XII CONCLUSIONS

The following specific conclusions have developed from the work with deoxidized vacuum sintered and arc-cast molybdenum:

1. Oxygen in the parent metal will cause hot cracking and porosity.
2. The harmful effects of oxygen in sintered molybdenum can be greatly reduced by the use of deoxidizers during vacuum sintering.
3. Carbon, tantalum, niobium and aluminum have not been found to be satisfactory for deoxidization of vacuum sintered molybdenum, and it is improbable that these materials should be used for arc-cast molybdenum where welding application is anticipated.
4. The ductility and soundness of weld beads in vacuum sintered titanium deoxidized molybdenum are comparable to the properties of welds in arc-cast material.

5. Use of titanium in the range 0.2-0.5% is advisable for welding applications.

6. The deoxidization method used in preparing titanium deoxidized vacuum sintered molybdenum is critical.

7. Titanium deoxidized vacuum sintered molybdenum shows better bend ductility than the carbon deoxidized vacuum sintered material.

The work with welding atmospheres led to a number of specific conclusions with regard to atmosphere requirements with respect to oxygen:

1. Oxygen concentrations in the welding atmosphere of 0.2% produce hot center bead cracking and cross cracks.

2. Oxygen in the welding atmosphere between 0.1 and 0.2% will probably produce both center bead and crater cracking.

3. Oxygen above 0.02% and below 0.05% will cause crater cracks in bead on plate welds.

4. As oxygen in the welding atmosphere is increased from 0.02% to 0.2%, the temperature for brittle failure increases.

5. The brittle failure strength decreases with increases in oxygen in the welding atmosphere.

6. The brittle failure strength vs. temperature curve for different oxygen contents in the atmosphere falls along the proportional limit vs. temperature curve for molybdenum.

7. Oxygen in the weld metal increases the temperature of brittle behavior from -150°F to 0°F between 0.004% and 0.007% oxygen in the weld bead.

8. The temperature at which maximum bend ductility, 100° bend angle, is obtained is moderately increased by oxygen below 0.1% but is drastically increased above this value.

Specific conclusions have been reached regarding welding atmosphere requirements with respect to nitrogen:

1. Nitrogen additions to the inert gas welding atmosphere in amounts up to 50% do not cause hot cracking or porosity.

2. Nitrogen in the welding atmosphere in amounts as small as 0.1% will cause a large increase in the nitrogen content of the weld metal.

3. It appears that 80% of the maximum possible amount of nitrogen acquired during welding can be obtained with nitrogen concentrations of 1% in the welding atmosphere.

4. Nitrogen in the weld beads increases the temperature at which complete ductility in the bend test can be achieved.

5. Reduction to a minimum of the combined percentage of elements capable of interstitial solution in the weld bead should reduce the temperature at which maximum ductility is obtained in the bend test.

6. Nitrogen lowers the fracture strength along the temperature vs. load at elastic limit curve but the change is smaller than was found for oxygen.

Nitrogen and oxygen interactions have indicated the following conclusions:

1. Nitrogen in the welding atmosphere reduces the tendency for oxygen to produce hot cracking in molybdenum weld beads.

2. When nitrogen and oxygen are added simultaneously to argon welding atmospheres, the amount of nitrogen acquired by the weld bead is a minimum at 2% N_2 and 0.2% O_2.

3. The amount of oxygen acquired by the weld bead is dependent upon the amount of nitrogen present in the atmosphere.

4. Oxygen and nitrogen in the welding atmosphere react in a manner by which each reduces the deleterious effects of the other.

5. While oxygen-nitrogen-argon mixtures give improved chemical and mechanical properties in molybdenum welds, they do not improve the properties beyond those found for welds made in high purity atmospheres.

Specific conclusions were reached with regard to heat treatment of molybdenum welds:

1. Heat treatment at 2000°C in vacuum reduces the nitrogen in the weld metal.

2. Heat treatment at 2000°C in vacuum causes precipitates to agglomerate and suggests improvement by an overaging process.

3. Stress relief for four hours at 900°C in vacuum appears to lower the temperature required for maximum bend deflection and for brittle failure.

4. Stress relief for four hours at 900°C in vacuum reduces the nitrogen in the weld bead from an expected 0.05% to 0.008%.

Straining prior to welding suggests these conclusions:

1. Welds made in arc-cast carbon deoxidized molybdenum prestrained 4% to 8% in tension at 300°F show no change in the bend ductility vs. temperature relationship as compared to unstrained welds.

2. Prestrained welds should be investigated to establish the inflection point found in the stress at proportional limit vs. temperature relationship.

Butt welds made in this period bring out the following conclusions:

1. Butt joints can be made using techniques available at present which show ductility equivalent to weld bead on a plate.

The specific conclusions may be briefly summarized by the following:

1. Deoxidizers for molybdenum have the following requirements: Nonvolatile at welding temperatures; nonvolatile oxides must be formed or products of deoxidization must be removed during fabrication; low melting point films from the deoxidizer or products of deoxidization must not be present in the grain boundaries; and precipitates formed by the deoxidizer or deoxidization product must not impede plastic deformation.
2. Titanium appears to meet the requirements for a deoxidizer.
3. Nitrogen, carbon, and oxygen must be eliminated or reduced to a minimum in the parent metal and welding atmosphere to obtain welds of maximum ductility.
4. Heat treatment may be used to reduce the nitrogen in the weld metal or to decrease its deleterious effects on weld ductility.

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APPENDIX I

DIAMETER OF CYLINDRICAL GRAIN OF LENGTH "ℓ" FOR COVERAGE BY MoO_2 AS A FUNCTION OF WEIGHT PERCENT OF MoO_2

Assume: Cylindrical grains in the weld center.

Where: d = diameter of grain

ℓ = length of grain

Assume the grains to be at 45° to the plane of the plate in a transverse section of the weld and 45° to the plate in a longitudinal direction. Then ℓ = f(t) where t is the plate thickness. Then $\ell = t\sqrt{3}$.

Area of cylindrical grain.

$$A = \pi d \ell + \frac{2\pi d^2}{4}$$

$$= \pi d \ell + \frac{\pi d^2}{2}$$

$$= \pi d (\ell + d/2)$$

This assumes oxide on both exposed faces but does not correct for the 45° projection on the surface from the circular diameter.

Unit cell of MoO_2 has following dimensions according to Wyckoff. The cell is monoclinic.

$$a = 5.610\ A^{\circ}$$
$$b = 4.843$$
$$c = 5.526$$
$$B = 119°\ 37°$$

Assume that the cells of MoO_2 have their basal plane parallel to the surface of the grain.

Then if β is the number of unit cells thickness of the MoO_2 film, the actual thickness is βc.

Thus, for a small thickness of MoO_2 film, the volume of the film would be

$$v = A\beta c = \beta c \pi d (\ell + d/2)$$

Volume of grain of diameter d and length ℓ is given as

$$V = \frac{\pi d^2 \ell}{4}$$

Relationship between wt.% MoO_2 and oxygen in the grain is as follows:

$$\frac{\frac{W_{MoO_2}}{128} \times 100}{100/96} = 1/2 \frac{\frac{W_o}{16} \times 100}{100/96}$$

$$\frac{W_{MoO_2}}{128} = \frac{W_o}{32}$$

$$W_{MoO_2} = 4\, W_o$$

Weight of molybdenum oxide per grain of Mo.

$v\,\delta = W_{MoO_2} \times \sim$ Where δ is density of MoO_2

$\sim$ is weight of a grain

$\sim = V\Delta$ where Δ is density of Mo

Then

$$v\,\delta = W_{MoO_2}\ V\,\Delta$$

$$v\,\delta = \delta\beta\ c\pi d(l + d/2) = \frac{\Delta\pi\ d^2 l}{4} W_{MoO_2}$$

$$\delta\beta\ c\pi l + \frac{\delta\beta\ c\pi d}{2} = \frac{\Delta\pi\ d l}{4} W_{MoO_2}$$

$$\frac{\Delta\pi\ d l W_{MoO_2}}{4} - \frac{\delta\beta\ c\pi d}{2} = \delta\beta c\pi l$$

$$\frac{d}{4}(\Delta l\ W_{MoO_2} - 2\delta\beta\ c) = \delta\beta c l$$

$$d = \frac{4\delta\beta\ c l}{\Delta l\ W_{MoO_2} - 2\delta\beta\ c}$$

$$d = \frac{4\delta\beta \quad c\ell}{\Delta \ell \ (4\ Wo) - 2\delta\beta c}$$

$$\ell = t\sqrt{3}$$

$$d = \frac{4\ \delta\beta\ ct\sqrt{3}}{\Delta t\sqrt{3}\ (4\ Wo) - 2\delta\beta c}$$

For material at hand

Δ = 10.2 gm/cm^3 for Mo

δ = 6.47 gm/cm^3 for MoO_2

c = 5.526×10^{-8} cm

t = .1521 cm (0.060" sheet)

d covers the range 0.025 to 0.075 cm

$$d = \frac{4 \times 6.47 \times 5.526 \times 10^{-8} \times .1521 \times 3\beta}{10.2 \times .1521 \sqrt{3}\ (4\ Wo) - \beta \times 2 \times 6.47 \times 5.526 \times 10^{-8}}$$

$$d = \frac{37.6 \times 10^{-8}\beta}{107\ Wo - 71.4 \times 10^{-8}\beta}$$

$$d = \frac{37.6\beta}{107 \times 10^{8}\ Wo - 71.4\beta}$$

$$107 \times 10^{8}\ Wo = \frac{37.6\beta}{d} - 71.4\beta$$

The second term on the right of the last equation accounts for oxygen on the exposed surface of the grain. It has been found that the error is small if this term is neglected.

Then

$$107 \times 10^{8}\ Wo = \frac{37.6\beta}{d}$$

$$\beta = \frac{107 \times 10^{8}\ Wod}{37.6}$$

Since Wo and β are related according to a linear function for any given value of d, it is possible to select a value of Wo = 0.01% and for a number of values of d compute points at Wo = 0.01 for β. These points may be connected with the zero point. Table I gives these points.

TABLE I

Grain Diameter d	Weight % O_2 W_o	Average Film Thickness $\beta = 107\ W_o\ d\ 10^8 / 37.6$
0.0125	0.01	3.59
0.025	0.01	7.18
0.050	0.01	14.35
0.075	0.01	21.5
0.100	0.01	28.7
0.125	0.01	35.9
0.150	0.01	43.1
0.175	0.01	50.2
0.200	0.01	57.5

Then at O_2 = 0.002%

d	β
0.025	1.5
0.075	4.5

and at O_2 = 0.004%

d	β
0.025	3.0
0.075	8.5

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